

# **A BITTER TRUTH**

ASTRINGENT PERSIMMON AS A BIO-ALTERNATIVE TO STANDARD

WOOD PRESERVATION TREATMENTS

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## ABSTRACT

A Bitter Truth:

Astringent Persimmon as a Bio-Alternative to Standard Wood Preservation Treatments.

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The elimination of pentachlorophenol in the 1980's, and the ban on chromated copper arsenate (CCA) as the preeminent wood preservative in 2004, brought a great deal of attention to wood preservatives and their impact on health and environmental safety. Currently, most wood preservatives are considered restricted pesticides, and their regulation makes very few products available for safe application on in-service materials. This also calls into question the ethics of using toxic and permanent preservatives on curated items such as historic building fabric.

This thesis discusses the potential for a sustainable bio-alternative wood preservative, derived from the astringent persimmon fruit of *Diospyros kaki*. Past research has identified and studied dozens of individual compounds in the genus *Diospyros*; many of these extractives are now known to be bioactive as fungicides, termiticides, antiseptics, and free-radical reducing compounds.

The genus *Diospyros* (syn. Persimmon, ebony) is widely distributed in most tropical and subtropical areas of both hemispheres with over 350 species, and a long cultural and agricultural history on several continents. A review of current literature shows a connection between the known traditional use of persimmon-derived coatings and the experimental use of persimmon tannin. The research presented in this thesis provides a preliminary review of two products as tested for both qualitative and quantitative properties. The tests sought to ascertain the character of the water resistant coating, the retention of the treatment, and their efficacy as a protectant against fungal sources. Visual studies on the color palette (and color variability with exposure to weathering) are also presented, along with observations on the interaction of these persimmon-derived products with iron oxide.

Droplet testing showed significant water resistance from the kakishibu as long as the coating is maintained; leaching tests indicated that kakishibu has comparable preservative permanence to the tested control, copper naphthenate. Soil-block culture analysis, despite the inconclusive mass loss data, provided valuable qualitative data on surface mold growth deterrence. The color variation tests showed a surprising result of darkening over time for the treatments, a feature that has been confirmed by textile artists working with kakishibu as a dye. The exploration of persimmon's reaction with iron oxide, common on iron fasteners in historic buildings, showed rapid visible change and a glossy well-adhered film with the raw juice, versus a less stable film with kakishibu. In summary, the forms of persimmon fruit studied in this research showed significant promise as bio-alternative wood preservative.

## **ACKNOWLEDGEMENTS**

This work would have been impossible without the help of my advisor, Norman Weiss, and my readers John Childs and Lori Arnold. I would like to also offer special thanks to Lori for not only support and information, but also a truly voracious fungal source.

I want to especially thank George Wheeler—without whom I would have been lost in navigating the intensive lab experimentation and possibly still in the stock room still searching for Büchner funnels—and my advisor Norman Weiss: without his insatiable curiosity, the topic of this study would never have been breached. Also, I would like to thank Nathan Carter and the staff of the Fabrication Lab for being so helpful in the sample fashioning process.

I dedicate this to my parents, who have always offered unfailing support and enthusiasm in my studies and in life. To my roommate, who put up with a freezer full of persimmons and cabinets of lab glassware for an entire year; to my family and friends, who understood the multitude of cancelled dates and missed parties; and to my amazing partner, without whom the final stretch would have been unbearable, sleepless, and bereft of her contagious enthusiasm.

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# CHAPTER 1: INTRODUCTION

## 1.1 ORIGIN OF CONCEPT

The beginning of the idea for this work is in great part to Norman Weiss, who introduced the possibilities of this topic in a class lecture based on his interest in wood extractives. His 1982 paper, "Wood Extractives as Wood Preservatives," with Frances Gale provided a springboard for delving into the connections between the realm of food science research/traditional medicinal methodologies involving persimmon trees and chemical assays on wood extractives from the *Diospyros* genus.<sup>1</sup> Hoping to find more contemporary research, I stumbled upon the same types of extractive information about Japanese persimmon—*Diospyros kaki*, the globally produced cousin of the American tree—as well as current U.S. and Japanese patents for persimmon derived insecticide.<sup>2</sup> This began the search into *Diospyros kaki*'s little known history as a traditional preservative, traditional medicine, and waterproofing agent. This confluence of traditional use and the science of modern pharmacology and chemical analysis opens a door into finding sustainable bio-alternatives for products disappearing from the market due to safety concerns.

In the building sciences there is an understood need for less toxic materials in buildings and in the environment due to the proven deleterious effects of many products we have

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<sup>1</sup> N.R Weiss, F.R. Gale, "Wood Extractives as Wood Preservatives," in *Conservation of Wooden Monuments, Proceedings of the ICOMOS Wood Committee, IV International Symposium*(Ottawa, ON1982).

<sup>2</sup> S. Yoshida, A. Igarashi. Insecticide Obtained from Plants for Use on Termites. 2003.

commonly used in the past. The wood working community has faced, and will continue to face, the increasing regulation of wood preservatives. Restrictions of popular preservative pentachlorophenol in 1987 and chromated copper arsenate (CCA) in 2004, were due to concerns of toxicity and environmental health, and likely represent an increasing potential for future regulatory action. This ongoing process of popular use and eventual regulation is what seems to be an accelerating cycle; especially with the modern understanding of pesticides resulting in mammalian toxicity through not just direct contact, but also long term accumulation in tissues. Along with the ever dwindling general list of available preservatives, the EPA labels most preservatives as "restricted" allowing their use only through pressure application by certified industrial registrants and leaving very few products for in situ application.<sup>3</sup>

These general concerns are exacerbated by conservation issues within preservation, where materials are historic, in-situ, and/or of highly selective character. Other conservation specific concerns include the irreversibility of a treatment or the permanent change to the chemistry of the wood, as well as the possibility of damage, staining, or loss to historic material as part of the preservation process. This significant preservative problem leads us to the search for alternate protection measures for wood through traditional means and new scientific research. Safer alternatives to preservatives are being explored, the most popular of

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<sup>3</sup> "Notice of Final Decision Concerning Reevaluation of Pesticide Products," ed. California Environmental Protection Agency Department of Pesticide Regulation(Sacramento, CA2005). & American Wood Protection Association, *A.W.P.A. Book of Standards*(Birmingham, AL: Thomson Reuters (Scientific) LLC, 2014).

which are boron compounds—commercially available termiticide and fungal deterrents that are considered non-toxic due to the natural occurrence of borates.<sup>4</sup>

Another option for safer wood preservation brings us back to the origin of this research: examining naturally occurring wood extractives that protect living wood. The high level of extractives in plants has traditionally been utilized in sap products; however, numerous compounds have been isolated from other basic extracts of tree products. It is from this second topic that the work for this thesis is derived.

## **1.2 TRADITIONAL PRACTICE & PHARMACOLOGY**

Traditional practices, or historical precedent, are often looked to in diagnosing historic building issues as well as in the proper methodology for repair. These methods, whose effectiveness has been proven with use and time, are often overlooked for scientific study outside of historical research. As natural practices, which are inherently sustainable in many regards due to their simple origins, traditional materials and methods can be looked to as a catalyst for expanding the field of bio-alternative practices in restoring historic works.

Folk medicine, a seemingly unrelated field, can actually provide many of the answers for the available uses of traditional bio-derived materials. Folk medicine, or alternative medicine, is a cultural healing practice that often expands beyond pharmacological means into wellness for the mind and body. The World Health Organization defines traditional medicine as “the sum of the knowledge, skills, and practices based on the theories, beliefs, and

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<sup>4</sup> It should be noted that there is still a substantial toxicity attributed to borate salts used in wood preservation, including sodium tetraborate (anhydrous borax); however, the EPA porting justifies the non-toxicity through naturally occurring boron content in vegetables.

experiences indigenous to different cultures, whether explicable or not, used in the maintenance of health as well as in the prevention, diagnosis, improvement or treatment of physical and mental illness.”<sup>5</sup> The diagnoses and uses of traditional medicines for the human body is part of a field called pharmacology—the study of the interaction of the human body with chemicals. It has provided numerous studies on how foods and traditional medicinal practices safely work within human health, including antibacterials, fungicides, and concentrated tannin compounds in dietary elements. Teas, grapes, and grape products—such as red wine—include polyphenolic non-flavonoid antioxidant compounds such as resveratrol and Gallic acid. These commonly serve as dietary antioxidants, but have often in the past been used for many other applications (Gallic acid being a major component in iron gall ink).<sup>6</sup>

### **1.3 CONSERVATION, LONGEVITY, AND STEWARDSHIP**

“Bio-alternative” and “sustainably sourced material” are buzzwords amongst a range of others tangled with the green movement, but what they reflect are traditional concepts that were norms before the introduction of industrial processing and the dominance of synthetic chemicals. These traditional methodologies should align seamlessly with the goals of the conservation of historic buildings, however without the research to prove its effectiveness—as both a method or product and in comparison to other available commercial means—these

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<sup>5</sup> World Health Organization, "General Guidelines for Methodologies on Research and Evaluation of Traditional Medicine,"(2000), 1.

<sup>6</sup> T. A. M. Msagati, "Preservatives," in *Chemistry of Food Additives and Preservatives*(Oxford, UK: Blackwell Publishing Ltd, 2012), 229.

traditions are left as just a part of history rather than finding applicability in the current market.

With the issues surrounding the toxic nature of many products commonly used to extend the life of wood, the availability of natural wood tannins as a preservative is a topic that should be of interest to both the general consumer of wood product as well as the wood and wooden objects conservation community. Tannins have been known to assist in the preservation of wood for an indefinite amount of time, with artifact fragments of wood strengthened with tannates having been found from at least the 12<sup>th</sup> century in Rouen, France and an extensive history of tannins in Japan that will be discussed later in this paper.<sup>7</sup> With no better way of saying it, natural wood extractives with termiticidal, biocidal, and fungicidal effects are of “supreme applicability to the conservation of wooden structures.”<sup>8</sup>

### **1.3.1 WHY WHAT WE USE TO PRESERVE MATTERS**

Minimally invasive techniques that respect authentic historic material have been prized since the Venice Charter<sup>9</sup>, therefore is it ethically sound to use preservative treatments that cannot be removed on authentic and adjoining replacement wood, treatments that require the removal of historic material, or pollute authentic material when we don’t fully understand the long term ramifications of a product?

In examining the ethical considerations of using wood preservative, The Nara Document on Authenticity, The American Institute of Conservation’s Code of Ethics, and the Principles for the Preservation of Historic Timber Structures issues by the International Council

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<sup>7</sup> M.A. Hatzfeld, "A New Process for the Preservation of Wood," *Popular Science Monthly* 5(1874).

<sup>8</sup> Weiss, "Wood Extractives as Wood Preservatives."

<sup>9</sup> Venice Charter, Article 9

on Monuments and Sites (ICOMOS) have assisted in better unifying the response to ethical considerations within the field of conservation regarding such as wood preservation. They are highly supportive of preventative conservation tactics, especially those that protect historic material while minimizing hazards to the public and the environment.<sup>10</sup>

One statement explained the accepted behavior of the current continued use of toxic preservatives instead of looking for other options. The AIC specify in Article 22 of the Code of Ethics that materials and methods should be consistent with currently accepted practice. The benefits of a material or method should be carefully balanced against the possible adverse effects and unknown long term issues. This is open to interpretation to a greater degree than the ICOMOS document which, as a wood specific paper, defines clearly that the principal intention of conservation is to maintain the historical authenticity and integrity of a cultural resource.<sup>11</sup> It continues by clearly defining wood preservation as a route to preserving as much as possible of existing material, where repair and replacement of material is acceptable when appropriate, if executed in matching species, and if not that, matching characteristics and physical features.<sup>12</sup> The principles in this document are forward thinking in establishing that the materials and methodology of how we repair and preserve wood buildings matter just as much as the wood itself. The principle of determining the long term ramifications of a preservation action is, instead of reverting to common practice, ensuring when engaging in an intervention that the process and end result should (in order or importance): follow traditional

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<sup>10</sup> AIC Article 1 & 12, ICOMOS Preservation of Timber Article 14

<sup>11</sup> ICOMOS Preservation of Timber Article 4

<sup>12</sup> Ibid Article 7

means, be reversible, not prejudice nor impede future work, and not obscure access to later investigation.<sup>13</sup>

### 1.3.2 LONGEVITY AND TOXICITY

An in depth understanding of material decay and the acceptance that replacement will occur to extend the building's life is required to analyze the expected longevity of a restored and maintained historic structure. In keeping as much historic material intact as possible to maintain integrity, processes to extend the life of extant material would be beneficial. With current products, this calls into question the ethics of using toxic and permanent preservatives on historic building fabric. This toxicity is not only permanently damaging to the wood, it poisons the surrounding environment and negatively effects inhabitant health through persistent accumulation.<sup>14</sup> While this immediately begs the question “why do we still use these,” the low cost, market familiarity, and well known effectiveness of these preservatives overrules green marketability and higher cost—incidentals of sustainable chemistry having not yet reached a norm in the science community. According to Jean Carroon's text on Sustainable Preservation: “In the United States, 4.1 billion pounds of known toxins were regulated and sold—12% of which are PBTs, persistent bioaccumulative toxins. These are not only toxins as a standalone product, but also accumulate in tissues and in the surrounding environment. Many pesticides fall into the PBT category.”<sup>15</sup>

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<sup>13</sup> Ibid Article 5

<sup>14</sup> M. Verma, S. Sharma, R. Prasad, "Biological Alternatives for Termite Control: A Review," *International Biodeterioration and Biodegradation* 63(2009).

<sup>15</sup> J. Carroon, *Sustainable Preservation: Greening Existing Buildings*(Hoboken, N.J.: Wiley, 2010).

# CHAPTER 2: WOOD IN HISTORIC PRESERVATION

## 2.1 MATERIAL CHARACTERISTICS

### 2.1.1 LENGTH OF LIFE

Wood has been widely used as a building material longer than our recorded history of its use, and in the right climate and circumstance can last hundreds of years in service; however wood cannot—even in ideal conditions—last forever. Distinctively, the Japanese developed their own traditions in wood construction that encompasses 90% of their current built heritage, which is in contrast to the many European sites whose wooden structures were readily replaced with predominance of brick and stone—a process carried into European colonialism.<sup>16</sup> With many uses in raw, engineered, and processed product and readily used as fuel, wood consumption has led to severe deforestation before the inception of sustainable forestry practice.<sup>17</sup> Sustainable building technologies often look to wood as a major material due to its access as a rapidly renewable resource and its predictability in physical and chemical change, however as a biological material it faces several common deterioration factors.

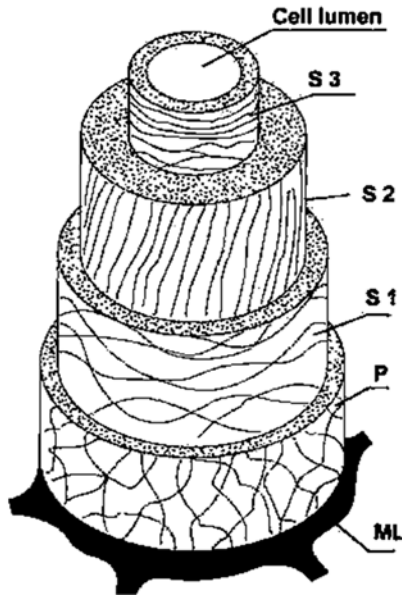
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<sup>16</sup> S.J. Kelley, J.R. Loferski, A. Salenikovich, E.G. Stern, ed. *Wood Structures: A Global Forum on the Treatment, Conservation, and Repair of Cultural Heritage* (Philadelphia, PA: American Society for Testing and Materials, 2000), vii.

<sup>17</sup> R.L. Youngs, "Wood: History of Use," ed. R.W. Cahn J.K.H. Buschow, M.C. Flemings, *Encyclopedia of Materials: Science and Technology* (Amsterdam: Elsevier Science, 2001).



Wood is composed of cellulose, hemicellulose, lignin, suberin, phenolic acids, and various extractives.<sup>18</sup> The structural polymers of wood are cellulose—which accounts for 40-50% of wood's dry weight, hemicellulose (25-40%), and lignin (20-35%).<sup>19</sup>



**Figure 1.** Wall structure and microfibril orientation in wood cells. Middle lamella (ML), primary cell wall (P), secondary walls (S1-S3), and cell lumen.[Deacon]

Cellulose and hemicellulose are the polysaccharides formed in glucose production of photosynthesis; cellulose is a long chain glucose whose structure allows for close hydrogen bonds, resulting in strong fibrous tissue, and hemicellulose is a branched chain polymer glucose that has a lower molecular weight. Lignin differs from the polysaccharides in that it is composed of high molecular weight amorphous phenylpropane polymers that form a matrix that acts as a glue binding together wood fibrils.<sup>20</sup>

Extractives are common for commercial products, including wood tar, syrups, rosins, oils, and tannins—the subject of this paper. These components are often the natural protection for wood and many other plants, providing characteristics that include color, odor, and bitter taste; however extractives are also attributed to the decay resistance of some species.<sup>21</sup>

Although there is a wide range of species specific determining factors, wood will deteriorate under natural circumstances differently in various climates, increasingly with the

<sup>18</sup> I. S. Goldstein, "Chemical Properties of Wood," in *Encyclopedia of Forest Sciences*, ed. J. Burley(Elsevier Ltd., 2004), 1835-36.

<sup>19</sup> J Deacon, *Fungal Biology*, (Blackwell Publishing, 2005).

<sup>20</sup> A. Zinc-Sharp, "Formation and Structure of Wood," in *Encyclopedia of Forest Sciences*, ed. J. Burley(Elsevier Ltd., 2004), 1809.

<sup>21</sup> Weiss, "Wood Extractives as Wood Preservatives," 138.

addition of water or soil contact. Forest Product Laboratory testing determined that control wood stakes of southern pine will last 1 year in tropical locations as determined by their site in Panama, 1.8-3.6 years in subtropical areas such as those at their test forests in Mississippi, Florida, and Louisiana, and 6 years in temperate areas such as their site in Wisconsin.<sup>22</sup>

### **2.1.2 HOW IT DETERIORATES**

Damage and failure of wood occurs through chemical decomposition, mechanical failure, biological attack, or some combination of the three. Chemical decomposition can occur naturally over time through age and exposure to light, but wood will also chemically decompose or change in the presence of high temperatures, ultraviolet radiation, and ionizing radiation. Hemicellulose begins degradation at temperatures greater than 120°C, lignin at greater than 130°C, and cellulose at greater than 160°C. Ultraviolet radiation, which is mildly unavoidable in exterior locations, forms free oxygen radicals that oxidize cells and preferentially deteriorate lignin, and ionizing radiation causes severe solubilization of wood polymers.<sup>23</sup> Free radical oxidization initializes several deleterious actions in wood including causing the aldehyde end groups in the chemical structure of wood polysaccharides to break down into carboxylic acids and other carbohydrates deteriorate into dicarboxylic acids. Aside from the cellular deterioration of the celluloses, the lower pH that results from the increase in acidic compounds provide a hospitable environment for fungal infection.<sup>24</sup> Oxidization results in the generation of hydroperoxides whose interaction with wood causes the

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<sup>22</sup> J. Blew, H. Davidson, "Comparison of Wood Preservatives in Stake Tests, 1969 Progress Report," (Madison, WI: US Department of Agriculture, Forest Service, Forest Products Laboratory, 1969).

<sup>23</sup> Goldstein, "Chemical Properties of Wood," 1838-39.

<sup>24</sup> F. F. P. Kollmann, W. Côté, *Principles of Wood Science and Technology*, vol. I. Solid Wood (New York: Springer-Verlag, 1968), 110.

depolymerization of the polysaccharide components.<sup>25</sup> Mechanical failure of wood is based on its directionally dependent strength and porosity. Factors that affect strength include the species of wood, the direction of grain in relation to stress, temperature, moisture content, and age. As an anisotropic material, tensile and compression strength are dependent on the direction of applied stress in relation to grain direction.

Wood has the most strength in tension parallel to the grain and the least strength in tension perpendicular to the grain; whereas compression strength is in the middle with more strength parallel to the grain compared to perpendicular.

Biological attack of wood structure is through a number of sources, but fungal and insect attack are of the greatest concern because of their prevalence and their blatant effect on the structure and aesthetic of affected wood. For instance, at 5-10% weight loss due to attack, wood strength can be reduced 20-80% of normal.<sup>26</sup> While there are numerous wood destroying insects—including carpenter ants, furniture beetles, powderpost beetles, deathwatch beetles—termite damage is extensive and common in wood construction. Termite attack is inversely proportionate to density or hardness of diffuse porous hardwoods, but is also waylaid by natural extractives in wood.<sup>27</sup>

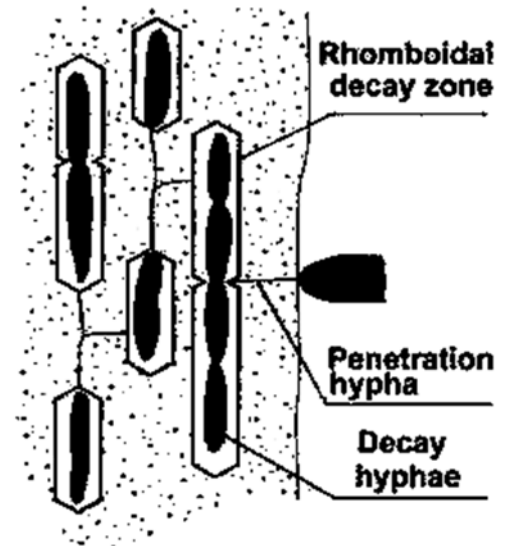


Figure 2. Diagram of hyphae penetration pattern for soft rot type fungi. Decay zones around hyphae due to enzymatic digestion. [Deacon]

<sup>25</sup> Goldstein, "Chemical Properties of Wood," 1837.

<sup>26</sup> S. Aganost, "Wood Decay, Fungi, Stain, and Mold," (Oneonta, NY: New England Kiln Drying Association, 2011), 25.

<sup>27</sup> E.A. Behr, C.T. Behr, L.F. Wilson, "Influence of Wood Hardness on Feeding by the Eastern Subterranean Termite, *Reticulitermes Flavipes*," *Annals of the Entomological Society of America* 65, no. 2 (1972):

Fungal growth can occur at greater 97% relative humidity or with free water present.<sup>28</sup>

The most common fungal infections are categorized into white rot, soft rot, and brown rot—each comprising of a vast number of fungal species that produce categorically similar effects on wood. Soft rot requires a damp environment to proliferate and grows throughout the lumen of the cells by entering through perforations in the lignin layer. It has little to no effect on the lignin of the wood, but concentrates on consuming the cellulose.<sup>29</sup> White rot results in a texture best described as “pulp” and unlike soft and brown rot, degrades the lignin of wood in an oxidative process (Figure 2).<sup>30</sup> Brown rot will degrade cellulose and hemicellulose through an oxidative process where hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) forms and passes through the lignin layer.<sup>31</sup> There is evidence that brown rot works through the fragmentation of cellulose by hydroxyl radicals (OH<sup>-</sup>). This is through free radical oxidation, a mechanism also prevalent in the degradation of lignin via white rot.<sup>32</sup>

### **2.1.3 HOW IT CAN BE REPAIRED**

Mechanical failure of wood due to stress requires immediate support before stabilization, repair, or replacement of the wood. If the systemic issue placing an abundance of stress continues, the support should remain in place to assist the historic material; however if mechanical failure is due to other reasons—such as other deteriorating factors or an

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457. & F.L. Carter, A.M. Garlo, J.B. Stanley, "Terminical Components of Wood Extracts: 7-Methyljuglone from *Diospyros Virginiana*," *Journal of Agricultural Food Chemistry* 26, no. 4 (1978): 873.

<sup>28</sup> Aganost, "Wood Decay, Fungi, Stain, and Mold," 27.

<sup>29</sup> Deacon, *Fungal Biology*.

<sup>30</sup> Aganost, "Wood Decay, Fungi, Stain, and Mold." Aganost 13 & Deacon, *Fungal Biology*.

<sup>31</sup> Ibid.

<sup>32</sup> B.L. Illman, D.C. Meinholtz, T.L. Highley, "Oxygen Free Radical Detection in Wood Colonized by the Brown-Rot Fungus *Postia Placenta*," in *Biodeterioration Research* (NY: US Department of Agriculture, Forest Service, Forest Products Laboratory, 1989).

incident—additional support may not be needed upon repair of the wood. Chemical decomposition and biological attack, which often produce the same deterioration characteristics, can often be repaired in the same way; the only major difference being chemical decomposition is often event or location based and biological attack is attached to the wood and has to be sterilized or disassociated before repair. Wood that has suffered loss can be kept in place and the structure reinforced through additional means, or the deteriorated wood can be repaired with epoxy or comparable consolidant. Replacement of the wood is an option, but the consequences of removing historic material should be heavily considered.

## **2.2 COMMON PRESERVATIVES**

The broad criteria of a wood preservative as outlined by the Forest Products Laboratory are (1) the product must protect the wood for the desired end use, and (2) they must not present an “unreasonable risk” to the environment and consumers. Wood preservative is classified as a pesticide and therefore its sale and distribution are regulated by the Environmental Protection Agency.<sup>33</sup>

### **2.2.1 LIST OF COMMON PRESERVATIVES**

Common preservatives applied through standard impregnation are waterborne or oil-borne (Table 1). The list of EPA approved wood preservative treatments for non-pressure application includes borates, oxine copper, zinc naphthenate, and copper naphthenate—a drastically

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<sup>33</sup> Forest Products Laboratory, "Wood Handbook—Wood as an Engineering Material,"(Madison, WI: US Department of Agriculture, Forest Service, Forest Products Laboratory, 2010).15-1

shorter list than the full spread of EPA approved wood preservatives. This is due to the classification of non-pressure application material needing to be consumer safe rather than their alternate classification, “restricted use.”<sup>34</sup> This is applied to preservatives that can only be handled by certified applicators, usually through pressurized impregnation.<sup>35</sup> In-place and remedial treatments for wood preservation include surface application (brush or spray) of a preservative, internal diffusion, and internal fumigation. Surface application will last approximately 1-5 years with approved treatments, and rely on manufacturer recommendations for reapplication protocol and scheduling.<sup>36</sup>

<b>Preservative</b>	<b>Solute</b>	<b>Application</b>
<i>Creosote</i>	N/A	Pressure Treatment
<i>Oxine Copper</i>	Hydrocarbon	Pressure Treatment, Surface Applied
<i>copper naphthenate</i>	Hydrocarbon, Water	Pressure Treatment, Surface Applied
<i>Pentachlorophenol</i>	Hydrocarbon	Pressure Treatment
<i>Borates</i>	Creosote, Water	Pressure Treatment
<i>Chromated Copper Arsenate</i>	Water	Pressure Treatment
<i>Alkaline Copper</i>	Water	Pressure Treatment
<i>Ammoniacal Copper Zinc Arsenate</i>	Water	Pressure Treatment
<i>Copper Azole</i>	Water	Pressure Treatment
<i>Alkyl Ammonium Compound</i>	Hydrocarbon, Water	Surface Applied

**Table 1.** Common wood preservatives, their fluid carriers, and method of application<sup>37</sup>

Borates are increasingly used as a wood preservative after the 2004 end of CCA usage.

Borates, while soluble, do not evaporate nor break down into inactive product and tend to

<sup>34</sup> Ibid.15-12

<sup>35</sup> Ibid. 15-2

<sup>36</sup> Ibid. 15-22

<sup>37</sup> American Wood Protection Association, *A.W.P.A. Book of Standards*.U1-14 Section 4

only have minimal migration from treated wood to the surrounding soil, less so with the addition of tannin flavonoids.<sup>38</sup> Borates work through their conversion to boric acid upon contact with acidic media (such as wood) and acts as a bait toxicant, but do not actively repel insects.<sup>39</sup> Borates are an effective fungicide and insecticide with minimal corrosive tendencies and mild fireproofing ability, and are also regarded as having minimal environmental impact.<sup>40</sup>

### **2.2.2 APPLICATION METHODS**

Methods of application for preservatives in an industrial setting is most often a vacuum impregnation process using heated preservative in an enclosed chamber.<sup>41</sup> The preservatives used in this process are regulated and unavailable outside of the pressure application process.<sup>42</sup> Instead, non-pressure applications are to be considered for the consumer use. These include soaking (flood coats), dipping, diffusion, brush application. These, due to minimal depth of penetration, are recommended for interior or protected uses.<sup>43</sup>

## **2.3 REGULATION OF WOOD PRESERVATIVES**

The overall responsibility for the regulation of preservatives falls to the U.S. Environmental Protection Agency, the federal entity that registers pesticides and their approved uses. This approval requires over 100 tests and applied studies to ensure the

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<sup>38</sup> G. S. Wieland Tondi, N. Lemenager, A. Petutschnigg, A. Pizzi, M. F. Thévenon, "Efficacy of Tannin in Fixing Boron in Wood: Fungal and Termite Resistance," *BioResources* 7, no. 1 (2012).

<sup>39</sup> M. Freeman, C. McIntyre, D. Jackson, "A Critical and Comprehensive Review of Boron in Wood Preservation," *American Wood Protection Association* Birmingham, AL(2008).

<sup>40</sup> G. Tondi, S. Wieland, M.F. Thévenon, A. Pizzi, T. Wimmer, A. Petutsching, "Tannin Boron Preservatives for Wood Buildings: Mechanical and Fire Properties " *European Journal of Wood and Wood Products* 70(2012).

<sup>41</sup> American Wood Protection Association, *A.W.P.A. Book of Standards*, 73.

<sup>42</sup> Forest Products Laboratory, "Wood Handbook—Wood as an Engineering Material."15-1

<sup>43</sup> American Wood Protection Association, *A.W.P.A. Book of Standards*, 69.

product safety or its categorization as “restricted use.”<sup>44</sup> In addition to the EPA requirements, state governments and their environmental protection agencies or departments of pesticide regulation can evaluate preservatives for safety concerns and require relabeling or discontinuance within the state.<sup>45</sup>

In addition to this, the Forest Products Laboratory of the U.S. Department of Agriculture constantly evaluates the effectiveness of preservatives through laboratory and field testing. Field stake testing began as an ongoing process in 1938 with the Forest Products Laboratory station at the Harrison Experimental Forest in Saucier, Mississippi.<sup>46</sup> Annual reports of ongoing decay rate calculations and effectiveness are available for all former and currently EPA approved preservatives in multiple available application methods.

### **2.3.2 OPPORTUNITY FOR OTHER PROCESSES**

The knowledge gained by testing of long term effects of preservatives has spawned legislation concerning the restriction and eventual halt of sale of several prominent preservatives including chromated copper arsenate, creosote, and pentachlorophenol. This, as well as a general hesitancy in the possibility of using products with unknown toxicity, has shaped the evaluative processes of governing agencies. The loss of such prominent preservatives allows for the experimental use of less toxic and unconventional bioactive preservatives including the topic of this thesis, concentrated tannins. In Denmark, which has both strong heritage protection and environmental protection laws, only borates and water-

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<sup>44</sup> Forest Products Laboratory, "Wood Handbook—Wood as an Engineering Material."15-1

<sup>45</sup> "Notice of Final Decision Concerning Reevaluation of Pesticide Products."

<sup>46</sup> B. Woodman, C. Hatfield, S. Lebow, "Comparison of Wood Preservatives in Stake Tests, 2011 Progress Report,"(Madison, WI: US Department of Agriculture, Forest Service, Forest Products Laboratory, 2011).



based fungicides are used to treat replacement timber through brush application or injection on existing wooden structures. However, these treatments are not applicable to use on buildings considered “highly significant” to Danish built heritage. Instead, non-destructive treatments including high frequency radio waves, micro waves, and hot air treatment are used to sterilize historic timber.<sup>47</sup>

Forest Product Laboratory stipulates that a wood preservative must (1) provide the desired wood protection in the intended end use and (2) must do so without presenting an unreasonable risk to the public or the environment.<sup>48</sup> This provides a sustainable cognizance to former lists available of typical ideal properties of wood preservatives that include items such as “high toxicity towards wood destroying organisms,” “permanence,” and “cheap and plentiful,” however with environmental and health concerns factored into the need for wood preservatives that are safe and effective, I propose these properties of an ideal wood preservative<sup>49</sup>:

- Effective in limiting future deterioration
- Applicable to all wood types
- Compatible with typical system materials (fastener metals, glues, finishes, etc.)
- Does not interfere with or impede other conservation activities
- Light stable
- Low VOC
- Low Toxicity
- Ease of use/application
- Adequate depth of penetration
- Moisture repellent
- Reversible and retreatable

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<sup>47</sup>O. Munck, J. Fode, "The Treatment of Fungal Growth in Heritage Structures in Denmark," in *Wood Structures: A Global Forum on the Treatment, Conservation, and Repair of Cultural Heritage*, ed. S.J. Kelley, J.R. Loferski, A. Salenikovich, E.G. Stern(Philadelphia, PA: American Society for Testing and Materials, 2000).

<sup>48</sup> Forest Products Laboratory, "Wood Handbook—Wood as an Engineering Material," 15-1.

<sup>49</sup> Composed in part using Food and Agriculture Organization of the United Nations: Forestry Division, "Wood Preservation Manual,"(1986), 35. and Wheeler, G. "Introduction to Consolidation" lecture 3.31.15

## CHAPTER 3: *DIOSPYROS*

### 3.1 HISTORY OF GENUS

*Diospyros*, of Greek nomenclature, the "fruit of Zeus" describing both the ambrosia flavor of the ripened fruit, and the blindingly sharp pucker of its unripe astringency.<sup>50</sup> The genus is found globally and produces both edible fruit and ebony wood within the spread of its more than 350 species.<sup>51</sup> The written history of this genus and its product is diverse and extensive, with recordings of persimmon varieties in the Americas described by conquistadors and English colonists, Indian persimmon was discussed by Virgil in writings concerning Ceylon, and Marco Polo recorded the heavy trade of persimmons in China.<sup>52</sup>

Kaki is common name in Asia and Europe for the fruit.<sup>53</sup> The word "persimmon" is actually derived from the anglicized versions of the Algonquin language group's word for the native fruit, which has been recorded as putchamin, pasimanan, and several others that come from the prefix 'pos' and suffix 'men'—a combination that, quite like the Greek derived genus

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<sup>50</sup> D.C. Peattie, "Persimmon," in *A Natural History of North American Trees* (New York: Houghton Mifflin, 2007), 458.

<sup>51</sup> U.V. Mallavadhani, A.K. Panda, Y.R. Rad, "Pharmacology and Chemotaxonomy of *Diospyros*," *Phytochemistry* 49, no. 4 (1998): 901.

<sup>52</sup> C.E. Bamford, "Persimmon," *The Independent*, May 16 1889; J.F. Morton, "Japanese Persimmon (*Diospyros Kaki* L.)," *Fruits of Warm Climates* (1987).

<sup>53</sup> A. Celik, S. Ercisli, "Persimmon Cv. Hachiya (*Diospyros Kaki* Thunb.) Fruit: Some Physical, Chemical and Nutritional Properties," *International Journal of Food Sciences and Nutrition* 59(2008).

title, translates to “choke fruit.”<sup>54</sup> The first physical description in English of the fruit was by Thomas Harriot in 1588, where he described them as a form of medlar—a common English fruit from the rose family with similar physical and chemical characteristics. His publication, "A Brief and true report of the new found land of Virginia" from his time as a surveyor with the Roanoke Colony, is the earliest English publication regarding the North American continent.<sup>55</sup> Harriot never specifically mentioned the taste or edibility of the fruit, aside from aligning them with medlars which also require ripening to be eaten due to astringency. The taste of the American Persimmon (*Diospyros virginiana*) was graphically described in A Map of Virginia, 1612, by Captain John Smith at Jamestown: "If it be not ripe, it will draw a man's mouth awrie [sic] with much torment."<sup>56</sup>

*Diospyros* grows within 45° North and South of the equator.<sup>57</sup> Growing conditions for the wood of the persimmon tree are best in primeval forest conditions where growth can be pushed to 100-130 feet. Optimal fruit growing conditions are for the trees to be spread out and seasonally docked to reduce the height. Even grown wild, trees remain small in diameter, not often growing greater than 1 ft. This greatly reduces its usefulness as large timber. Climate change and environmental impact of settling has greatly reduced the widespread nature of

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<sup>54</sup> C.H. Briand, "The Common Persimmon (*Diospyros Virginiana* L.): The History of an Underutilized Fruit Tree (16th -19th Centuries)," *Huntia* 12(2005): 73-74; M. Kurlansky, *The Food of a Younger Land: A Portrait of American Food*(New York: Riverhead, 2009).

<sup>55</sup> Briand, "The Common Persimmon (*Diospyros Virginiana* L.): The History of an Underutilized Fruit Tree (16th -19th Centuries)," 72.

<sup>56</sup> Peattie, "Persimmon." 458

<sup>57</sup> Celik, "Persimmon Cv. Hachiya (*Diospyros Kaki* Thunb.) Fruit: Some Physical, Chemical and Nutritional Properties." 600

North American species of persimmon; for instance, *Diospyros oregana*'s once natural habitat was the Pacific Northwest, however it can now only be found in a remote location in Java.<sup>58</sup>

### 3.1.1 PROPERTIES OF *DIOSPYROS*

There is a large amount of crossover between species within *Diospyros* regarding their extractives and their associated properties; as such, there are possibilities for extractives to be present in species that have not been assayed with specific intent.<sup>59</sup>

Historic uses for the fruit of *Diospyros*—other than in raw ripened or dried—are commonly based around its high glucose content when ripened to use in food items such as brandy, beer, sweet bread, and a sugary quince-like paste. In the United States, the prevalence of *D. virginiana* in the confederacy during the Civil War prompted creative re-use of native traditions including medical antiseptic tonics made from the roots, leaves, and bark of the tree and juices from the fruit. Embargo prevented easy access to luxury items and seeds of American Persimmon were able to be ground for a coffee substitute, barks were used as dyes, and the green unripe fruit were used to make gall ink.<sup>60</sup> Aside from its uses as an antiseptic, persimmon has been used as an astringent, treatment for uterine hemorrhage, dysentery, diphtheria, dropsy, fever, gonorrhoea, syphilis, and thrush.<sup>61</sup> Natives and early European settlers to the southern states used persimmon to treat bowel concerns and symptoms of dysentery.<sup>62</sup>

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<sup>58</sup> Peattie, "Persimmon."

<sup>59</sup> Carter, "Terminicidal Components of Wood Extracts: 7-Methyljuglone from *Diospyros Virginiana*." and references therein; Mallavadhani, "Pharmacology and Chemotaxonomy of *Diospyros*."

<sup>60</sup> Briand, "The Common Persimmon (*Diospyros Virginiana* L.): The History of an Underutilized Fruit Tree (16th -19th Centuries)," 71,79.

<sup>61</sup> Ibid.

<sup>62</sup> Peattie, "Persimmon."

Extractives from the *Diospyros* genus are a rich source of triterpenes, naphthoquinones, and naphthalene derivatives.<sup>63</sup> Compounds isolated from *D. virginiana* include 7-methyljuglone and several dimers that are highly toxic to termites.<sup>64</sup> Plumbagin (2-methyl-hydroxy-1, 4 naphthoquinone) is attributed to the termiticidal and vesicant properties of several tropical *Diospyros* species.<sup>65</sup> The ebonized heartwood of persimmon shows greater termite resistance however this is likely due to extractives as well as wood hardness<sup>66</sup> *D. virginiana* has shown moderate resistance to the termite *Reticulitermes flavipes*.<sup>67</sup> 1, 4-naphthoquinones show fungicidal activity for both germination inhibition and against impregnation tests and naphthalene derivatives from *D. assimilis* (ebony) inhibit protozoan parasites.<sup>68</sup> Aside from *D. assimilis*, several other persimmon species show ebonized characteristics that are naturally resistant to fungal and termite attack.<sup>69</sup> Antifungal metabolites were also extracted from *D. virginiana*; more found in root structure than found in leaf and wood analysis.<sup>70</sup>

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<sup>63</sup> Carter, "Termiticidal Components of Wood Extracts: 7-Methyljuglone from *Diospyros Virginia*." 869

<sup>64</sup> Ibid. 871, 873

<sup>65</sup> Ibid. 872

<sup>66</sup> Ibid. 873; Behr, "Influence of Wood Hardness on Feeding by the Eastern Subterranean Termite, *Reticulitermes Flavipes*." 458

<sup>67</sup> F.L Carter, T.R. Dell, "Screening Selected American Hardwood for Natural Resistance to a Native Subterranean Termite, *Reticulitermes Flavipes*," (New Orleans, LA: US Department of Agriculture, Forest Service, Southern Forest Experiment Station, 1981). 4

<sup>68</sup> N.G. Clark, "The Fungicidal Activity of Substituted 1,4-Naphthoquinones," *Pesticide Science* 5, no. 1 (1984); S. Ganapaty, P.S. Thomas, S. Fotso, H. Laatsch, "Antitermitic Quinones from *Diospyros Sylvania*," *Phytochemistry* 65, no. 1 (2004).

<sup>69</sup> E. Noda, T. Aoki, K. Minato, "Physical and Chemical Characteristics of the Blackened Portion of Japanese Persimmon (*Diospyros Kaki*)," *Journal of Wood Science* 48(2002).

<sup>70</sup> X. Wang, E. Habib, F. Leon, M. M. Radwan, N. Tabanca, J. Gao, D. E. Wedge, S. J. Cutler, "Anti-Fungal Metabolites from the Roots of *Diospyros Virginia* by Overpressure Layer Chromatography," *Chemistry of Biodiversity* 8, no. 12 (2011).

The fruit of the persimmon tree is relatively delicate and as damaged material is not sold as produce, other uses must be found for damaged stock.<sup>71</sup> Skin blackening, a natural defect, as well as shallow cracking also make fruit unmarketable.<sup>72</sup> The loss from this has resulted in study for alternate uses to minimize economic loss, for example Gorinstein et al. used fluorometric analysis of *D. kaki* to determine if phenolics could be extracted for alternative uses; however there is little other research dedicated to waste diversion for persimmon.<sup>73</sup>

### **3.2 HISTORY OF JAPANESE PERSIMMON, D. KAKI**

*Diospyros kaki*, commonly known as the Japanese persimmon, is native to Japan, China, Burma, and India, but most likely originated in China.<sup>74</sup> *D. kaki* has been included as a feature in Chinese garden landscaping since the Heian Period (794-1185 CE) and has religious and cultural significance in Asian culture.<sup>75</sup> Persimmon is known to be used in religious and traditional cultural ceremony to imbue success on various endeavors. Superstition dictates that persimmon trees were planted to keep fires away, using the wood for fuel causes insanity, and dreaming of eating persimmons while gravely ill means death is near.<sup>76</sup> In a personal

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<sup>71</sup> S. Gorinstein, M. Zemser, M. Weisz, S. Halevy, J. Deutsch, K. Tilis, D. Feintuch, N. Guerra, M. Fishman, E. Bartnikowska, "Fluorometric Analyses of Phenolics in Persimmons," *Bioscience Biotechnology and Biochemistry* 58(1994).

<sup>72</sup> M. Yamada, E. Giordani, K. Yonemori, "Persimmon," in *Fruit Breeding*, ed. M. Badenes and D. H. Byrne (New York: Springer, 2012). 683

<sup>73</sup> Gorinstein, "Fluorometric Analyses of Phenolics in Persimmons."

<sup>74</sup> Morton, "Japanese Persimmon (*Diospyros Kaki* L.)."

<sup>75</sup> A. R. Deane, "Appendix C: Common Flora," *Japanese Gardens Online Handbook* (2012), [www.japanesegardensonline.com](http://www.japanesegardensonline.com).

<sup>76</sup> J. Vegder, "Glossary: J through Kakure-Gasa," *Prints of Japan*, [www.printsofjapan.com/Index\\_Glossary\\_J\\_thru\\_Kakuregasa.htm](http://www.printsofjapan.com/Index_Glossary_J_thru_Kakuregasa.htm).

account of a trip to Japan, Norman Weiss witnessed a temple replacing its roof in traditional methods—often a part of Japanese culture in retaining the integrity of the building as well as its sacred nature—and learned of their tradition of brushing the ends of the rafters with persimmon juice. It is unknown if this is a sacred process or one borne from materials tradition.

### **3.2.1 PHYSICAL PROPERTIES**

*D. kaki* typically is 4.5-18m in height, 4.5-6 m in canopy spread. Leaves are typically oblong, 7.5-25cm long 5-10cm wide. Deciduous, color is blue green in spring/summer and changes to yellow orange red during autumn. Calyx shape and size depends on species; similarly, seed content is dependent on cultivar and pollination type. Pollination requires only one male tree to eight female, with 12-24 trees and 1-2 bee hives per acre for healthy production, otherwise can be hand pollinated. Propagated in root stock and seeds, however due to long maturation cycle is most often propagated in root stock.<sup>77</sup> Persimmon trees are very hardy and can withstand both drought and excessive ground moisture. In drought conditions, there is a decrease in fruit quality and yield; inversely, *kaki's* ability to withstand excessive ground moisture is maximized if grafted onto *D. lotus* or *D. virginiana* root stock.<sup>78</sup> Most pest and disease risk is negligible with *D. kaki*; the only noted exception is a susceptibility to crown gall (*Bacterium tumefaciens*) that can be minimized with the prevention of injury to the trunk and

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<sup>77</sup> Morton, "Japanese Persimmon (*Diospyros Kaki* L.)."

<sup>78</sup> J.H. LaRue, K.W. Opitz, J.A. Beutel, "Growing Persimmon," ed. University of California Division of Agricultural Sciences(Berkley, CA1982).6

crown roots.<sup>79</sup> Timber from Japanese persimmon is heavy and coarse grained; good for carving, furniture, and ornament.<sup>80</sup>

### 3.2.2 GLOBAL DISTRIBUTION

Several *Diospyros* species have been cultivated for thousands of years in Eastern Asia, but global distribution of *D. kaki* has only occurred within the last two centuries.<sup>81</sup> *D. kaki* was introduced to Australia in 1885 and the eastern Mediterranean in 1912, and later southern Europe.<sup>82</sup>

Emergence of the Japanese persimmon in the American market was after its introduction by Commodore Matthew Perry in 1855 after opening trade with Japan.<sup>83</sup> Japanese and Chinese cultivars of *D. kaki* for agriculture were first introduced to California in 1870.<sup>84</sup> Although it takes up to ten years for trees to reach full yield potential, the regularity of fruit production, fruit size, and the extended availability for transportation before ripeness of astringent *kaki* dominated native persimmon in the American market.<sup>85</sup>

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<sup>79</sup> Ibid. 7

<sup>80</sup> H. Loomis, "Farm and Garden: The Japanese Persimmon," *The Independent*, March 29 1877.

<sup>81</sup> Celik, "Persimmon Cv. Hachiya (*Diospyros Kaki* Thunb.) Fruit: Some Physical, Chemical and Nutritional Properties." 599

<sup>82</sup> Morton, "Japanese Persimmon (*Diospyros Kaki* L.)."

<sup>83</sup> Kurlansky, *The Food of a Younger Land: A Portrait of American Food*.

<sup>84</sup> LaRue, "Growing Persimmon." 3

<sup>85</sup> Ibid. 3, Briand, "The Common Persimmon (*Diospyros Virginiana* L.): The History of an Underutilized Fruit Tree (16th -19th Centuries)." 84



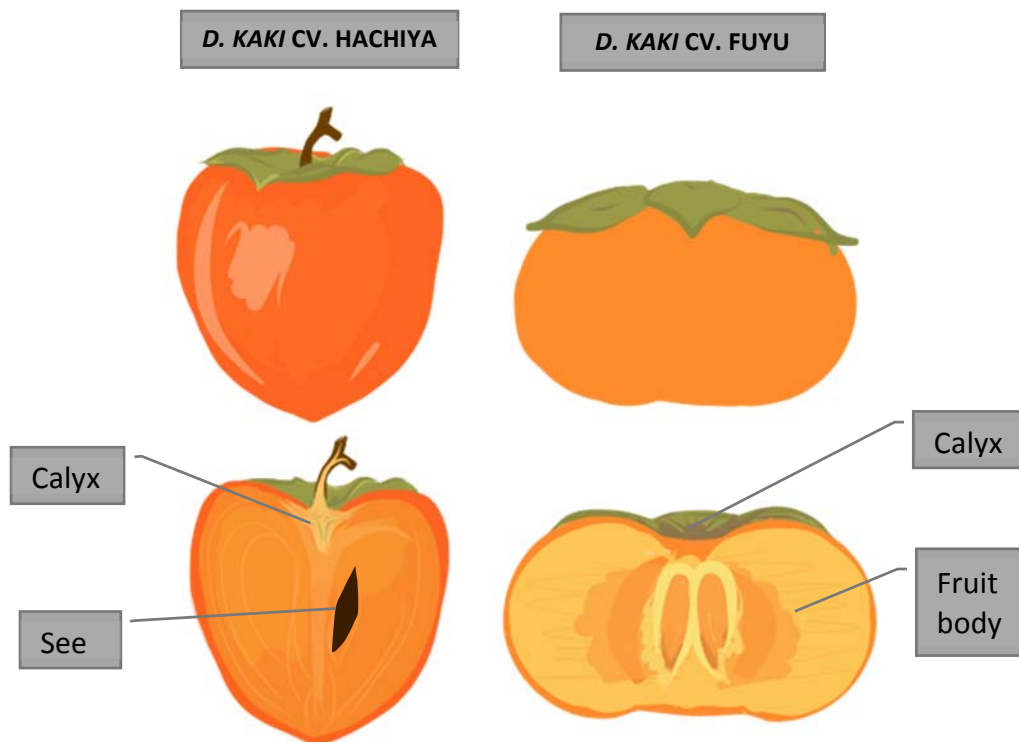


Figure 3. Basic anatomy of the *Diospyros kaki* fruits from cultivars Hachiya (the focus of this study) and Fuyu

### 3.2.3 CULTIVARS

There are four standard classifications for persimmon cultivars: pollination constant non-astringent (PCNA), pollination constant astringent (PCA), pollination variant non-astringent (PVNA), pollination variant astringent (PVA). These are based on the nature of the fruit's astringency.<sup>86</sup> Seeds in pollination variant cultivars exude acetaldehyde and ethanol, both mechanisms of ripening.<sup>87</sup> Acetaldehyde causes tannins to become insoluble and oxidized, and ethanol has also shown an ability to decrease ripening time.<sup>88</sup> Pollination constant non-astringent varieties, such as the common Fuyu cultivar, stop tannin accumulation

<sup>86</sup> S. Kanzaki, K. Yonemori, A. Sugiura, A. Sato, M. Yamada, "Identification of Molecular Markers Linked to the Trait of Natural Astringency Loss of Japanese Persimmon (*Diospyros Kaki*) Fruit," *Journal of the American Society of Horticultural Science* 126, no. 1 (2001).

<sup>87</sup> Yamada, "Persimmon." 664

<sup>88</sup> Morton, "Japanese Persimmon (*Diospyros Kaki* L.)."

early in its fruit development, resulting in non-astringent fruit regardless of seed presence.<sup>89</sup> The first pollination constant non-astringent variety, “gosho”, was first mentioned in the 17<sup>th</sup> century and originated in the Nara prefecture of Japan.<sup>90</sup>

### 3.2.4 HACHIYA

The Hachiya cultivar of *Diospyros kaki*, the common astringent variety, is the subject of this thesis testing. In a 1982 report, the Hachiya was the most popular cultivar of persimmon; however in recent years the Fuyu cultivar has drastically increased its popularity due to its non-astringency and lower ripening time.<sup>91</sup> Hachiya fruit’s physical properties, on average, are 6cm long, 6.5 cm diameter, approximately 170g with a 0.4mm skin thickness.<sup>92</sup> The chemical and nutritional value of 100g of Hachiya shows an acidic pH and approximately 17% measurable solids (Table 2).<sup>93</sup>

<b>pH</b>	5.4	±	0.28
<b>Total Soluble Solids</b>	17.10 %	±	1.10%
<b>Protein (g)</b>	0.6	±	0.07
<b>Ash (g)</b>	0.44	±	0.06
<b>Potassium (g)</b>	0.203	±	0.02416
<b>Phosphorus (g)</b>	0.027	±	0.00266
<b>Calcium (g)</b>	0.016	±	0.00433
<b>Magnesium (g)</b>	0.011	±	0.0018
<b>Sodium (g)</b>	0.010	±	0.0008
<b>Tannins (g)</b>	0.00315	±	0.00022
<b>Iron (g)</b>	0.00027	±	0.00008
<b>Manganese (g)</b>	0.00025	±	0.00004
<b>Coper (g)</b>	0.00011	±	0.00003
<b>Zinc (g)</b>	0.00010	±	0.00002

Table 2. Chemical and nutritional value of 100g of *Diospyros kaki* cv. Hachiya

<sup>89</sup> Kanzaki, "Identification of Molecular Markers Linked to the Trait of Natural Astringency Loss of Japanese Persimmon (*Diospyros Kaki*) Fruit."

<sup>90</sup>Yamada, "Persimmon." 669

<sup>91</sup> LaRue, "Growing Persimmon." 4, Kanzaki, "Identification of Molecular Markers Linked to the Trait of Natural Astringency Loss of Japanese Persimmon (*Diospyros Kaki*) Fruit."

<sup>92</sup> Celik, "Persimmon Cv. Hachiya (*Diospyros Kaki* Thunb.) Fruit: Some Physical, Chemical and Nutritional Properties." 603

<sup>93</sup> Ibid. 604

## 3.3 HISTORY OF USE

### 3.3.1 PRODUCE

In China, the first harvest of persimmon is hard fruit that can be cured through processes including cold cure, smoke cured, vinegar soak, or a boiling water dip with two day water soak. Water soaks can be lime water, which can reduce early rotting and disinfect the fruit. In Japan, hard fruit is cured through ethanol spray, storage in former sake kegs, three days ethylene gas exposure<sup>94</sup>, or 24 hours in a 95% CO<sub>2</sub> atmosphere.<sup>95</sup>

Harvest ready fruit will develop a rich orange color and semi-translucent skin, and fully ripened fruit is significantly softened and will fall from the tree naturally. A traditional process of collecting and preserving persimmons is through an intensive air drying process. This dried persimmon, *Hoshigaki*, is still being hand crafted by traditional methods in Japan and in the Central Valley and southern California.<sup>96</sup> Aside from the fruit and fruit product, fish was traditionally preserved for storage and transport to the interior of the island by wrapping in persimmon leaves. *Kakinoha-zushi*, a sushi of pickled mackerel wrapped in persimmon leaves, is still available in the Nara prefecture today.<sup>97</sup>

### 3.3.2 PERSIMMON TANNIN

Persimmon tannins take the form of processed juice and its aged product, kakishibu. Persimmon tannin and kakishibu are traditional material in China and Korea, but found a more

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<sup>94</sup> Ethylene gas is given off by ripening fruit such as bananas, pears, tomatoes, and apples

<sup>95</sup> Morton, "Japanese Persimmon (*Diospyros Kaki* L.)."

<sup>96</sup> R. Blumberg, J. Campos, N. Cole, B. Lewis, C. Moravec, M. Paine, H. Ricks, "Hoshigaki: Preserving the Art of Japanese Hand-Dried Persimmons," (Berkley, CA: University of California Sustainable Agriculture Research and Education Program, 2004). 6

<sup>97</sup> J. and N. Palevsky Kinoshita, *Gateway to Japan*, Third ed. (New York: Kodansha International, 1998).

prolific life in Japan. Raw pressed tannins from persimmon start as a milky green/yellow color that when exposed to ultraviolet light, heat, and oxygen, darken to a darker walnut color.<sup>98</sup> Tannins from unripe persimmons are used in brewing sake, dyes, wood preservatives, and insect and moisture repellent.<sup>99</sup> Kakishibu, as a traditional coating, was recently tested with other traditional Japanese treatments and is not a fire-resistant or fire-proofing agent.<sup>100</sup>

In *nuri*, the Japanese art of lacquering, persimmon tannin is used to harden polishing cloths in the traditional method as well as use as a finishing treatment.<sup>101</sup> Persimmon juice is applied to boards using a standard *urushi* brush, a common lacquering brush (fig. x), as a base when lacquer is to be transparent as to show the natural wood grain.<sup>102</sup> This is also used to waterproof the board so lacquer will not be absorbed in later *nuri* work that uses *urushi*, a traditional plant based lacquer.<sup>103</sup> *Sumi*, lampblack or charcoal, was used in combination with persimmon juice in *shibu-ji* (*shibu-sumi-nuri*) lacquering for the groundwork of cheap articles.<sup>104</sup> Many of the Japanese wood carvings and ephemera supposed to be walnut at the centennial exhibition in Philadelphia were actually common wood stained with persimmon.<sup>105</sup>

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<sup>98</sup> Personal Communication with B. Whitehead

<sup>99</sup> Morton, "Japanese Persimmon (*Diospyros Kaki* L.)."

<sup>100</sup> M. Akizuki, Y. Hasemi, K. Kinoshita, K. Yammamoto, M. Yoshida, Y. Tamura, M. Takeda, "Fire Safety Studies in the Restoration of a Historic Wooden Townhouse in Kyoto – Fire Safety Experiments on Japanese Traditional Wood-Based Constructions " (paper presented at the 5th AOSFST, Newcastle, AUS, 2001). 339

<sup>101</sup> C. Eades, Y. Nishiyama, Y. Hiroko, *The Work of the Lacquerer (Nurishi)*, (2008), [hdl.handle.net/10367/141](http://hdl.handle.net/10367/141). 19

<sup>102</sup> *Ibid.* 12, 22

<sup>103</sup> *Ibid.* 53

<sup>104</sup> "Report by Her Majesty's Acting Council at Hakodate on the Lacquer Industry of Japan," (London: Harrison & Sons, 1882). 10

<sup>105</sup> Loomis, "Farm and Garden: The Japanese Persimmon."



Figure 4. Kakishibu process, from crushing the immature persimmons (i) to its soak in water (ii) and week or more fermentation (iii) before being squeezed for the raw juice (iv) that will age to become Kakishibu

### 3.3.3. KAKISHIBU

Aged persimmon tannin is a traditional material used in furniture making, dyeing, and wood preservation, but as a traditional material with a localized culture of use, there are no experts or “bibles” to persimmon dyeing like there are with indigo and many other natural dyes.<sup>106</sup> Kakishibu is sold as a specialty and DIY product throughout Japan in garden shops and hardware stores; however, the product develops a disagreeable odor from the formation of butyric acid.<sup>107</sup> Mokume dashi, a furniture lacquering process, uses kakishibu’s reddish tones as a base and red dye component where the color is intended to contrast with the sumi treated black framework.<sup>108</sup> Kakishibu is also used in making traditional katagami stencils for fabric dyeing and dyeing cloth—a product called shibuzome.<sup>109</sup>

Bryan Whitehead, a textiles artisan living in Japan and working with traditional materials and methods, has been interested in kakishibu for several years:

<sup>106</sup> B. Whitehead to Japanese Textile Workshops 19 August 2012.

<sup>107</sup> J. J. Rein, *The Industries of Japan* (New York: A.C. Armstrong & Son, 1889). 182; J. Feurpeil to 90 Days in Kyoto: Journal of a Japanese garden apprentice Apr 24, 2014.

<sup>108</sup> Eades, *The Work of the Lacquerer (Nurishi)*. 51

<sup>109</sup> Vegder, "Glossary: J through Kakure-Gasa."

“You run across articles on persimmon tannin processing in magazines and musty old journals on Japanese crafts. Inevitably the used-for-a-single-week-a-year hand-cranked fruit/persimmon squasher [sic] is pictured in a corner of a smelly barn along with rustic bamboo baskets overflowing with green persimmons. [...] The process is described but the real secrets of the trade, like how long the fruit is allowed to ferment and how it is filtered etc. are always left conspicuously out.”<sup>110</sup>

The general process for kakishibu is during the early summer, green persimmons are crushed in iron mortars, moved to wooden tubs, and covered with water for a day. This is then pressed through cloth and then in a press to yield juice. There are two grades, first press and second press. The juice darkens over air exposure time for several years and the product provides marked toughness to papers, fabrics, and wood.<sup>111</sup> One coat of kakishibu on kozo paper<sup>112</sup> will increase its strength but also its brittleness. It requires several applications to increase the plasticity of the paper until it develops a leathery texture and pliable stiffness.<sup>113</sup>

### 3.3.4 TRADITIONAL MEDICINE

Persimmon tannin has deep roots as a traditional medicine all over the world; especially in China and Japan. Shi Di (*kaki* calyx), Shi Gen (*kaki* root), Shi Qi (immature *kaki* fruit juice), Shi Ye (*kaki* leaf), and Shi Zi (*kaki* fruit) are all traditional Chinese medicines used for calming the liver, clearing heat, resolving toxins, staunching bleeding, gastric issues,

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<sup>110</sup> B. Whitehead to Japanese Textile Workshops 27 September 2010.

<sup>111</sup> Rein, *The Industries of Japan*. 181

<sup>112</sup> Kozo is a traditional thin paper made from the inner bark of the paper mulberry tree (*Broussonetia papyrifera*)

<sup>113</sup> L. Goodman, "More Than What You Wanted to Know About Kaki-Shibu," *World of Washi Newsletter* 8, no. 2 (2002).

engendering liquids in the body (for clearing lungs and pericardial effusion), relieving cough or asthma, dysentery, heat stroke, hiccough, hypertension, internal bleeding, and oral lesions.<sup>114</sup> Kaki-yô is a traditional Japanese medicine made from the leaves of *D. kaki* that is used for hypertensive conditions.<sup>115</sup> The condensed tannins in persimmon leaf tea are also known to decrease blood pressure; this may be due to the major polyphenols in persimmon leaves being water soluble condensed tannins that are easily extracted in a tea infusion process.<sup>116</sup> The fruit of *D. kaki* is known by Japanese doctors as a preservative and blood purifier, much in the same way as the grape or wine cure of Southern Europe.<sup>117</sup>

Working off the knowledge that persimmon tannins are a traditional Japanese medicine to prevent stroke and reduce hypertension, recent medical research shows that crude persimmon tannin significantly inhibits stroke and prolongs lifespan in SHRSP (spontaneously hypertensive, stroke prone rats).<sup>118</sup> Crude persimmon tannin is also known as a potent antioxidant and scavenger of free radicals—the active oxygen species related to inflammation, carcinogenesis, arteriosclerosis, and aging.<sup>119</sup>

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<sup>114</sup> J. Zhou, G. Xie, X. Yan, *Encyclopedia of Traditional Chinese Medicines : Molecular Structures, Pharmacological Activities, Natural Sources and Applications*, vol. 6(Berlin: Springer, 2011).

<sup>115</sup> G. Chen, H. Lu, C. Wang, K. Yamashita, M. Manabe, S. Xu, H. Kodama, "Effect of Five Triterpenoid Compounds Isolated from Leaves of *Diospyros Kaki* on Stimulus-Induced Superoxide Generation and Tyrosyl Phosphorylation in Human Polymorphonuclear Leukocytes," *Clinica Chimica Acta* 320(2002).

<sup>116</sup> K. Kawakami, S. Aketa, H. Sakai, Y. Watanabe, H. Nishida, M. Hirayama, "Antihypertensive and Vasorelaxant Effects of Water-Soluble Proanthocyanidins from Persimmon Leaf Tea in Spontaneously Hypertensive Rats," *Bioscience, Biotechnology, and Biochemistry* 75, no. 8 (2011). 1435

<sup>117</sup> Loomis, "Farm and Garden: The Japanese Persimmon."

<sup>118</sup> S. Uchida, H. Ohta, I. Sekine, R. Edamatsu, M. Hiramatsu, A. Mori, G. Nonaka, I. Nishioka, M. Niwa, M. Ozaki, "Effects of Persimmon Tannin on the Prolongation of Life Span of Shrsp and on Active Oxygen Free Radicals," *Japanese Heart Journal* 29, no. 4 (1988).

<sup>119</sup> Ibid.

### 3.3.5 AGRICULTURE

*D. kaki* is a global agricultural crop with harvest regions on every continent. Trees most often require 3-6 years for yield, with young trees produce 22-40kilos per year while seasoned trees (10+ years) can produce 150-250 kilos annually. First harvest takes place in fall/ early winter and second harvest takes place after first frost.<sup>120</sup> China is the lead producer of Japanese persimmon, and the U.S. is only a minor producer with growth mainly limited to California, which accounts for 99% of U.S. persimmon product.<sup>121</sup> Global production of persimmon has almost doubled in the last decade, increasing from 2,500,000t (2005) to 4,600,000t (2013).<sup>122</sup>

<b>Country</b>	<b>Tonnage</b>	<b>Global Production</b>
<i>China</i>	3,618,823	78%
<i>Korea</i>	351,990	7.6%
<i>Japan</i>	214,700	4.6%
<i>Brazil</i>	173,169	3.7%
<i>Azerbaijan</i>	143,106	3.1%
<i>Other</i>		3%

Table 3. Global percent production, FAO. Other includes, but not restricted to, Uzbekistan, Italy, Israel, New Zealand, Iran, Nepal, Slovenia, Australia, and Mexico

Agricultural production of persimmons in the United States is not reported by the statistics bureau at the Food and Agriculture Organization, nor are the statistics available through the USDA as a single entity—instead persimmons are included in a minor category of “Misc. Fruit and Nuts.” The only available recent statistic is from the San Diego agriculture report that lists 1380t produced in 2013. Due to the increase in global consumption

<sup>120</sup> Morton, "Japanese Persimmon (*Diospyros Kaki* L.)."

<sup>121</sup> R.J. Collins, A.P. George, A.D. Mowat, "The World Trade in Persimmons," *Chron. Horticulture* 33(1993); Blumberg, "Hoshigaki: Preserving the Art of Japanese Hand-Dried Persimmons." 11

<sup>122</sup> Food and Agriculture Organization of the United Nations: Statistics Division, "Food and Agricultural Commodities Production: Persimmons,"(2013).



persimmon, the market for quick edibility has resulted in the current persimmon breeding goals by programs in Korea, Italy, and Spain are non-astringency, appearance, ripening time, post-harvest preservation, and disease resistance.<sup>123</sup>

### 3.4 ARCHITECTURAL APPLICATION

Information concerning the architectural application of kakishibu is less readily available than information of its use in furniture and other lacquerware. Many guides and histories of Japan make references to the black castles of Japan being “painted” black, but there are only a few anecdotal references to the makeup of the paint. It is most likely that this black paint is a compound of persimmon tannin and pine ash. This coating, called shibu-sumi-nuri, is much like the coating used in lacquerware. It’s known to be used at Kumamoto Castle, an early 17<sup>th</sup> c. fortress at the base of Mount Aso.<sup>124</sup> There is also a possibility the blackened exterior could be from another method for wood preservation called Shou-sugi-ban, a traditional acetylated process. With the knowledge that the black coating used to protect the exterior of the black castles could originally—and currently if restored with traditional materials—be persimmon tannin based, there are several other structures to examine. Other feudal era castles with this coating have been identified as: Matsue, Matsuyama, Matsumoto, and Okayama castles. Kakishibu is also reemerging in contemporary design. An Atelier Tekuto project—“Boundary House”—lists kakishibu as an interior wood finish. Japanese architect Terunobu Fujimori has

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<sup>123</sup> Yamada, "Persimmon." 663

<sup>124</sup> "Japan Cities Guide: Kumamoto," <http://www.japanvisitor.com/japan-city-guides/kumamoto-guide>.

also employed traditional techniques such as kakishibu in his work. His book, *Journey on Materials*, is on evoking traditional material uses.<sup>125</sup>

### 3.5 PHARMACOLOGY

There are a large number of seemingly unrelated chemical studies in food science and pharmacology that help lead to hypotheses about viability of persimmon tannin use. For instance, the types of tannins and phenols found in persimmon are similar to those in white oak and red wines, and have comparable uses in protein binding and medically beneficial effects.<sup>126</sup> Connections such as this need to be further examined as interdisciplinary crossover can assist in locating substances with similar properties to a known preservative. Table 4 shows several compounds found in *D. kaki* and their pertinent properties.

<i>Location</i>	<i>Compound</i>	Antibacterial	Antifungal	Antioxidant	Insecticide
<i>Fruit</i>	Hydrolyzable Tannins: Gallic Acid	X	X	X	
	Condensed Tannins			X	
	Plumbagin				X
	Lycopene			X	
	Isoquercitrin	X		X	
<i>Wood</i>	Borates		X		X
	7-methyljuglone				X
<i>Leaves</i>	Hydrolyzable and Condensed Tannins	X	X	X	
	Ursolic Acid	X			
	Oleanolic Acid			X	
	Myricetin	X			

**Table 4.** Partial chemotaxonomy of *D. kaki*; shows prevalent antibacterial, antifungal, antioxidant, and insecticide compounds

<sup>125</sup> See Further Reading for details

<sup>126</sup> Jackson

### 3.5.1. ANTIBACTERIAL AND FUNGICIDAL EFFECTS ON HUMAN DISEASES

Kaki extractives are highly antiviral. Professor Tadashi Shimamoto has discovered that *kaki* tannin is anti-noroviral and has patented a safe and comfortable skin disinfectant using *kaki*. The tannin is also shown to—in vitro—effectively destroy 20 other viral pathogens including influenza H3N2, influenza H5N3, herpes simplex v-1, vesicular stomatitis, sendai, new castle disease, poliovirus, coxsachievirus, adenovirus, rotavirus, feline calicivirus, and norovirus.<sup>127</sup> This could be a result of the content of 1, 4-naphthoquinones and derivatives that show high antimicrobial and antifungal activity that supersedes oxacillin, a penicillinase-resistant antibiotic.<sup>128</sup>

### 3.5.2. TANNINS AND REDUCTION OF FREE RADICALS

Tannins are found throughout the *Diospyros* genus, and the large amount of tannins in the unripe PCA and PVA cultivars of fruit linger until ripening of fruit renders tannins as insoluble crystals.<sup>129</sup> Tannins, from the colloquial "tanning" process in which they were widely used, are phenolic compounds of sufficiently high molecular weight as to precipitate and bind proteins, starches, cellulose, and minerals. They are often found in plant structures requiring natural protection from destructive agents, including buds, leaves, roots, seeds, and stem tissues.<sup>130</sup> Tannins have several distinguishing characteristics including: free phenolic groups, a

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<sup>127</sup> K. Veda, R. Kawabata, T. Irie, Y. Nakai, Y. Tohya, T. Sakaguchi, "Inactivation of Pathenogenic Viruses by Plant-Derived Tannins: Strong Effects of Extracts from Persimmon (*Diospyros Kaki*) on a Broad Range of Viruses," *PLOSONE* 8, no. 1 (2013); "Interview with Professor Tadashi Shimamoto," Hiroshima University Graduate School of Biosphere Science, [www.hiroshima-u.ac.jp/en/gsbs/interview/Shimamoto](http://www.hiroshima-u.ac.jp/en/gsbs/interview/Shimamoto).

<sup>128</sup> I. Buchkevych, M. Stasevych, V. Chervestova, R. Musyanovych, V. Novikov, V. Poroikov, T. Glorizova, D. Filimonov, G. Zagoriy, M. Ponomarenko, "Computational and Antimicrobial Studies of New 1,4-Naphthoquinones Aminothiazole Derivatives," *Cheminè Technologija* 61, no. 3 (2012).

<sup>129</sup> Mallavadhani, "Pharmacology and Chemotaxonomy of *Diospyros*." 901

<sup>130</sup> A. Cannas, "Tannins: Fascinating, but Sometimes Dangerous Molecules," Cornell University, Department of Animal Science, [www.ansci.cornell.edu/plants/toxicagents/tannin.html](http://www.ansci.cornell.edu/plants/toxicagents/tannin.html).

molecular weight from 500 to above 20,000, with few exceptions they are soluble in water, and have the ability to bind proteins to form tannin-protein complexes.

There are two forms of tannin, hydrolyzable tannins and proanthocyanidins, more commonly known as condensed tannins.<sup>131</sup> Hydrolyzable tannins are hydrolyzed by mild acids or bases, hot water, or enzymes to yield carbs and phenolic acids. They are usually present in small quantities in plant material. Condensed tannins are oligomers or polymers of flavanol, and are more common than hydrolyzable tannins. The acid catalyzed reaction of condensed tannins creates an array of red anthocyanidin pigments that are responsible for the non-chlorophyllic colors in plants and are also responsible for plant astringency. Tannins are able to form complexes with many types of molecules including carbohydrates (starch and cellulose are especially reactive to condensed tannins), proteins, and bacterial cell membranes. Insoluble protein tannins are formed when tannins are present in excess. This creates a hydrophobic surface layer.<sup>132</sup>

<b>Wood preservative compounds</b>	<b>Location found on <i>Diospyros</i></b>
<b>Tannins</b>	Fruit, leaves
<b>Aromatics</b>	Fruit, root, bark
<b>Flavanoids</b>	Fruit, leaves, root, sapwood
<b>Terpenoids</b>	Fruit, leaves, seeds, root, bark, ebonized wood, heartwood,
<b>Naphthoquinones</b>	Fruit, leaves, root, bark, heartwood

Table 5. Known preservative compounds assayed in *D. kaki* and their source.<sup>133</sup>

Tannins act as a natural plant defense to fungal attack, bacterial colonization, and consumption. Tannins react and perforate the cell wall of rumen bacteria, rendering them

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<sup>131</sup> Ibid.

<sup>132</sup> Ibid.

<sup>133</sup> Mallavadhani, "Pharmacology and Chemotaxonomy of *Diospyros*." 908

unable to digest tannin containing material.<sup>134</sup> Tannins are toxic to several known bacterial and viral strains through metal ion inhibition, enzyme inhibition, and destruction of cell membranes.<sup>135</sup>

Use of tannins as a wood preservative is not a new concept. In 1874, Adolphe Hatzfeld suggested using “acid tannate of peroxide of iron” as a preservative. He theorized that tannins would have a similar ability to bind proteins in vegetable matter as it does with animal tissues in the tanning process. His observation that we get many of our tanning solutions from the extractives of trees such as white oak and chestnut provides a vital link in the conceptualization of creating processes to imbue other trees with analogous natural protective properties. Hatzfeld also cites an 1830 examination of oak from a 12<sup>th</sup> century bridge at Rouen that was ebonized through the aging of an application of tannate of peroxide of iron.<sup>136</sup>

*D. kaki* is known as a potent antioxidant and scavenger of free radicals—known for their destructive effect on biological material (see section 2.1.2).<sup>137</sup> Other than tannins, the availability of antioxidant phenolic compounds may be the cause of persimmon's effectiveness against free radical damage.<sup>138</sup>

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<sup>134</sup> Cannas, "Tannins: Fascinating, but Sometimes Dangerous Molecules".

<sup>135</sup> Ibid.

<sup>136</sup> Hatzfeld, "A New Process for the Preservation of Wood."

<sup>137</sup> Uchida, "Effects of Persimmon Tannin on the Prolongation of Life Span of Shrsp and on Active Oxygen Free Radicals."

<sup>138</sup> H.S. Ahn, T.I. Jeon, J.Y. Lee, S.G. Hwang, Y. Lim, D.K. Park, "Antioxidant Activity of Persimmon and Grape Seed Extract: In Vitro and in Vivo," *Nutrition Research* 22(2002). 1271

### 3.5.3. HIROSHIMA AND NAGASAKI ORAL HISTORY

Another interesting phenomenon related to the medicinal uses of persimmon tannin is the use of persimmon as a folk remedy after the bombing of Hiroshima and Nagasaki. Oral histories of commonly relate that persimmon tannin or persimmon tea was administered in great quantity to survivors. Shuntaro Hida, who in 1945 was a medical officer at Hiroshima Military Hospital, recounts in his memoir a local remedy using wet leaves that seemed effective on severe burn victims, and later discusses the effective use of a local “superstition”—persimmon leaves—in saving the lives of many from radiation sickness.<sup>139</sup>

Sumiteru Taniguchi, a young man at the time of the destruction of Nagasaki, was severely burnt and suffered radiation sickness in the aftermath. In his interview with *People’s Century*, he discusses a folk remedy of persimmon leaf tea that was provided to assist in his body’s detoxification.<sup>140</sup> Chiyoko Egashira, another survivor of Nagasaki, cites the use of persimmon leaf tea as a method of regaining her health after suffering radiation sickness.<sup>141</sup>

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<sup>139</sup> S. Hida, *Under the Mushroom-Shaped Cloud in Hiroshima—a Memoir*, (2006), [www.wcpeace.org/Hida\\_memoir.htm](http://www.wcpeace.org/Hida_memoir.htm). 7, 12

<sup>140</sup> "Interview with Sumiteru Taniguchi, Japanese Citizen, Nagasaki," *People’s Century: Fallout, 1945-1995*.(1995), [www.pbs.org/wgbh/peoplescentury/episodes/fallout/taniguchitranscript.html](http://www.pbs.org/wgbh/peoplescentury/episodes/fallout/taniguchitranscript.html).

<sup>141</sup> "The Memory of That Day," in *Testimonies of the Atomic Bomb Survivors*.(Nagasaki Broadcasting Company Nov. 25, 1970 to Jan. 3, 1973 (rebroadcast in entirety, Jan 10 1995)).

## CHAPTER 4: RESEARCH DESIGN

The intention of the laboratory testing sequence was to determine how well the persimmon treatments fit the ideal preservative qualities as mentioned in [2.3.2 Opportunity for other processes](#). This exploration of persimmon as a possible wood preservative was intended to provide a preliminary review of both the quantitative analysis of persimmon's typical preservative features, as well as qualitative visual studies for its suitability as a conservation material.

In order to perform these tests as efficiently and expediently as possible with the available resources and fitting within the time frame available, it was necessary to develop alternate preparation procedures as well as accelerated methods for determining the viability of the persimmon tannin as a wood preservative.

The scope of standards by the American Wood Preservation Association (AWPA) closest aligned to testing viability of preservatives is instead to ascertain decay by selective fungi<sup>142</sup> or to determine minimum required pound per square foot of a known preservative.<sup>143</sup> These are also tested through vacuum impregnation of the preservative into the wood—the common industrial preservative method—but make no allowances to test for applicability of surface applied coatings. This is most likely an undeveloped area due to the suggested use of surface

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<sup>142</sup> American Wood Protection Association, *A.W.P.A. Book of Standards*. 445 E10-12

<sup>143</sup> *Ibid.* 456

applied coatings being restricted to use categories 1, 2, and 3A—interiors and coated exterior constructions—which are at lowest risk for deterioration.<sup>144</sup>

Another issue is the extended time frame for deterioration testing, a known problem that has been examined at great length to ascertain accelerated methodology. The National Institute of Food and Agriculture ran a program from 2006-2010 that identified a need to create reliable accelerated methods to design environmentally safe wood preservatives. Other concerns issued in the study include cost effectiveness and issuing changes to the AWPA standards. This resulted in the creation of AWPA Standards E20—Standard method for Determining the Depletion of Wood Preservatives in Soil Contact, E22—Standard Accelerated Laboratory Method for Testing the Efficacy of Preservatives Against Wood Decay Fungi Using Compression Strength, E23—Accelerated method of Evaluating Wood Preservatives in Soil Contact, E27—Standard Field Test for Evaluation of Wood Preservatives to be Used Above Ground; Accelerated Horizontal Lap Joint Test (bending stiffness as a measure of biodegradation).<sup>145</sup> This work, as well as the AWPA Standard E10-12 standard method of testing wood preservatives by laboratory soil-block cultures and AWPA Standard E11-12 standard method for accelerated evaluation of preservative leaching, drove the development of an experimental pathway to ascertain—within the constrained timeline of this thesis—the viability of persimmon tannin as a surface applied preservative.

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<sup>144</sup> Ibid. 69

<sup>145</sup> D. Nicholas, "Development of Accelerated Test Methods for Evaluating Wood Preservatives for Use in above Ground Applications," (Mississippi State, MS: Forest and Wildlife Research Center, Department of Forest Products, 2010).



## **4.1 MATERIALS**

Materials chosen for testing were in consideration of ASTM and AWWA standards, availability, and to determine applicability to historic substrate. More importantly, the substrates listed below were chosen to give a more accurate representation of the effect of the treatments on all wood seen in conservation, not just new material.

### **4.1.1 SEASONED MATERIAL**

Material 1 is an eastern white pine (*Pinus strobus*) purchased as interior grade millwork and seasoned indoors for approximately five years. Board chosen was quarter-sawn, of even coloration, with regular growth rings and no knots.

### **4.1.2 WEATHERED MATERIAL**

Material 2 is an eastern white pine (*Pinus strobus*) purchased as interior grade millwork and weathered outdoors in a carpenter's storage rack (no ground contact, partially covered conditions) for approximately five years. Board chosen was quarter-sawn, with regular growth rings and no knots. Patina was even in coloration and depth throughout selected cuts.

### **4.1.3 HISTORIC MATERIAL**

Material 3 is a historic material sourced from a loft floor board in a barn on the Jones property in Owego, NY. Age of the sample is approximately 150 years based on known construction on the property. Identification and observations concerning the sample are noted in Appendix D.

#### **4.1.4 METAL**

An unmodified Cor-Ten sample with a rich patina coating was used to determine reaction of persimmon treatments with in-situ iron products. Hypothetically, the tannin content of persimmons will produce a tannic acid-type reaction and a darker coating.

### **4.3 TREATMENTS**

#### **4.3.1 RAW PERSIMMON JUICE**

After sufficient examination of traditional method and recommendations for tannin examination, a raw juice product was decided on for the application of persimmon tannin. In sample preparation, the fresh preparation of materials was determined to be best for tannins, however samples can also be freeze dried for extended storage. Temperatures of greater than 60°C may cause heat damage and polymerization, and care was taken to avoid certain solutes as acetone can inhibit the tannin-protein interaction.<sup>146</sup>

Eight pounds (8 lbs.) of tree harvested Hachiya cultivar persimmon were acquired from Exeter, CA in early October. The fruit were yellow-orange, firm; based on availability at the time. Early fruit from late summer would have maximized the available astringency as is done traditionally, however first harvest astringent fruit in October has the highest tannin content and aligns with the goals of finding a secondary use for blemished unmarketable product.<sup>147</sup>

Fruit were hand processed using a thin steel box grater and juiced through cheese cloth to produce 800mL of juice that was jarred, sterile sealed, and refrigerated at 35°F until used;

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<sup>146</sup> Cannas, "Tannins: Fascinating, but Sometimes Dangerous Molecules".

<sup>147</sup> Mallavadhani, "Pharmacology and Chemotaxonomy of Diospyros."920

pH measured at 5-5.5. Pulped material and sliced fresh samples were flash frozen and retained for any miscellaneous future analysis or replication of original material.

#### **4.3.2 KAKISHIBU**

Due to shipping restrictions and a lack of availability in the United States, liquid kakishibu is often unavailable to the general American consumer. Instead, 25g of concentrated Kakishibu powder was purchased from WetPaint, a textiles and paper dye retailer. Product was prepared, as directed, with water to produce full strength Kakishibu (0.05g/mL)<sup>148</sup> which was diluted 25% and 50% to produce testing dilutions (0.0375g/mL; 0.025g/mL); pH measured in the 3-4 range.

#### **4.3.3 COPPER NAPHTHENATE**

copper naphthenate (CuN), is a commercially available surface applied wood preservative that has waterborne and hydrocarbon-borne varieties. Although considered safe for general consumer use, products were re-evaluated for indoor use due to claims of illness due to off-gassing. CuN gained a significant foothold in the market after the ban on penta and then later after the ban on CCA, however it is beginning to be heavily investigated by the EPA. As of 1997, the use of CuN products indoors was no longer supported by the EPA and is the product is required to carry the label “for exterior use only.” A respirator is obligatory for extended application exposure.<sup>149</sup> This treatment was chosen as the control comparison due to its availability, its carrier, as well as its position within the regulatory environment.

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<sup>148</sup> Full instructions available in Appendix D

<sup>149</sup> "Notice of Final Decision Concerning Reevaluation of Pesticide Products."4

Because of its consumer availability and use as a brush applied preservative, a CuN product was chosen as a comparative control. COPPER-GREEN® Brown Wood Preservative was the specific CuN product acquired for use in the testing.<sup>150</sup>

## **4.4 OVERVIEW OF TESTING PROCEDURES**

### **4.4.1 SCHEDULE**

Allotted time for materials acquisition and testing, given the term schedule at Columbia (approx. 15 weeks), was significantly less than desired to perform full ASTM procedures (min. 20 weeks), long term weathering tests, or field tests (>1 year). Accelerated methods available were evaluated and did not meet desired requirements for the evaluation of persimmon as a viable preservative; therefore methods were derived for this thesis that fit within the available timeframe and meet desired goals.

### **4.4.2 METHODOLOGY**

Basic methodology is working from a control comparison for all tests to determine observational data concerning the efficacy of persimmon tannin across several defined strata—both quantitative and qualitative—listed below. Controls are untreated wood of each substrate and a control treated with copper naphthenate, an established preservative that is able to be surface applied in the same manner as the persimmon treatments.

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<sup>150</sup> MSDS available in Appendix D

#### 4.4.3 QUANTITATIVE

##### *Contact Angle & Surface Absorption*

To determine the hydrophobic properties or wettability of each treatment, a contact angle test using a droplet method was performed on all samples applied to the radial face and on persimmon tannin and pure kakishibu applied to the end grain of a seasoned board (Material 1). The test was photographed and filmed for analysis in playback.

As an extension of the droplet method used for the contact angle analysis, surface absorption was measured for more exact analysis of coating failure. This was used in place of ASTM D5401-03: Standard Test Method for Evaluating Clear Water Repellent Coatings on Wood.

##### *Leaching Test*

The leaching test followed the recommendations set forth by the AWPA and ASTM for the preservative permanence analysis or leaching of a waterborne wood preservative.

##### *Soil Block Culture*

The soil block culture test as recommended by the AWPA and ASTM standards was modified to fit the available time frame of the thesis schedule. Instead of culturing pure samples of certain fungi as defined by the sample, an actively infected wood sample was scavenged for serviceable material. As this test is more to determine whether or not persimmon tannins are viable as a protective coating or deterring measure against fungal attack—not to ascertain specifics of a known preservative—this was determined to be an acceptable modification.<sup>151</sup>

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<sup>151</sup> Specifications can be found in Appendix D

#### **4.4.4 QUALITATIVE**

Visual studies conducted were observations on color palette and possible color change or variation in interior exposure, a short term exterior weathering to determine visual treatment retention, and an observational analysis of the reaction of persimmon product with iron oxide on Cor-Ten. Theoretically, the persimmon tannin should have the same or similar effect as tannic acid on iron oxides, creating an iron tannate conversion layer that is a stable coating.

# CHAPTER 5: METHODOLOGY

## 5.1 CONTACT ANGLE & SURFACE ABSORPTION

To determine the resistance of each surface applied treatment to water, the approximate contact angle and surface absorption of water in contact with treated surfaces were evaluated. Surfaces tested were on radial and transverse seasoned wood and treated with kakishibu or raw juice. Test was conducted by depositing a water droplet on each test surface using a pipette. Measurements were taken on radial and transverse surfaces using 2mL and 1mL volume drops respectively. Each was analyzed at advancing contact angle upon formation of droplet through direct observation, basic photography, and filming for secondary analysis.

Surface absorption was measured through the same process with the time for absorption or evaporation starting with the deposit of the water onto each surface during the contact angle test and ending with the surface of each sample being clear of free water. The results are defined as percent deviance, in excess or deficit, from the evaporative control on a watch glass of a 1mL (transverse surface test) or 2mL (radial surface tests) of water.

## 5.2 LEACHING TEST

Leaching test is based on ASTM D1413-07-13—Leaching Test and Preservative Permanence<sup>152</sup> with the only modification being the initial treatment of the 19 mm cubes of

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<sup>152</sup> See Appendix

sample wood by dipping in the solution for 30 minutes rather than the suggested vacuum impregnation of the preservative. Samples were left to dry and condition for four days in the lab environment before being stored until testing. Samples grouped by preservative treatment and covered with 200mL deionized water. Initially run for 30 minutes in vacuum desiccator to fully saturate sample with water, before the leach water is drained off and particulate solution collected through a Büchner funnel on no.2 Whatman filter paper<sup>153</sup>, oven dried at 115°C, and weighed. Process repeated at 6 hour, 24 hour, 48 hour, 7 days, and 14 days. Results charted and tabulated quantitatively, photo-documentation of each leach cycle recorded for qualitative analysis. Samples then dried in ambient lab environment for seven days before reweighing and calculating treatment loss.

### **5.3 SOIL BLOCK TEST**

ASTM D1413-07-0 Standard Test Method for Wood Preservatives by Laboratory Soil Block Cultures used as a guideline for the methodology of this testing sequence.<sup>154</sup> The scope for ASTM D1413-07 is to determine minimum effective amounts of preservative against fungal decay of a known preservative to facilitate subsequent tests for effectiveness against termites in ASTM D3345 and field tests using stakes in ASTM D1758. The test measures a failure to protect as evidenced by loss of wood from treated blocks, typified by loss of weight. The test method has been modified to guide the testing of a treatment of unknown viability as effective in any regard against fungal decay, measured in loss of material compared to loss in an untreated control.

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<sup>153</sup> Product Specifications available in Appendix

<sup>154</sup> See Appendix



As with the procedure in the leaching test, samples were dipped in treatment solutions for 30 minutes rather than the suggested vacuum impregnation to better simulate an in-situ brush or flooding application of wood preservative. Sample blocks were then exposed to the open lab environment for four days to dry and reach moisture equilibrium.

The sample blocks were organized into treatment groups, based on narrowest margin of measured density. Each group consists of 2 duplicate bottles, and treatments consist of: Kakishibu ( $K_p$ ), Kakishibu 25% dilution ( $K_{25}$ ), Kakishibu 50% dilution ( $K_{50}$ ), raw persimmon juice (Raw), an untreated control, and a copper naphthenate (CuN) control, applied to seasoned, weathered, and historic substrates.



Figure 5. Treated 19mm cube samples arranged by jar number. Excluding the last row to the right, each set of four is (clockwise from upper left) kakishibu, raw juice, copper naphthenate, and untreated.

The organization of all 72 samples into 18, 32oz French Square bottles is tabulated below.

<i>Jar</i>	<b>A1</b>	<b>A2</b>	<b>B1</b>	<b>B2</b>	<b>C1</b>	<b>C2</b>
<i>Sample #</i>	<b>1-12</b>	<b>13-24</b>	<b>25-36</b>	<b>37-48</b>	<b>49-60</b>	<b>61-72</b>
<i>Seasoned</i>	$K_p$ Raw CuN Control	$K_p$ Raw CuN Control	$K_{25}$ Raw CuN Control	$K_{25}$ Raw CuN Control	$K_{50}$ Raw CuN Control	$K_{50}$ Raw CuN Control
<i>Weathered</i>	$K_p$ Raw CuN Control	$K_p$ Raw CuN Control	$K_{25}$ Raw CuN Control	$K_{25}$ Raw CuN Control	$K_{50}$ Raw CuN Control	$K_{50}$ Raw CuN Control
<i>Historic Material</i>	$K_p$ Raw CuN Control	$K_p$ Raw CuN Control	$K_{25}$ Raw CuN Control	$K_{25}$ Raw CuN Control	$K_{50}$ Raw CuN Control	$K_{50}$ Raw CuN Control

Sample bottles were constructed by drilling two holes for air into the cap before gluing filter paper into the underside for assisting in moisture control. Each jar was then filled half-way with sterilized potting soil moistened to 150% of saturation, and then one inch of infected fungal wood and detrital matter. Sample treatment groups were then placed into their appropriate jars and incubated for 12 weeks in a dark enclosed box with care to avoid temperature decrease below 80°F. Observations of each jar were noted at the 6 week mark, and at the end of incubation, blocks were removed from the jars and left to dry for 1 week. Each set was photographed and brushed clean before the weight of each sample was evaluated for loss and visual evidence of decay.

## **5.4 VISUAL STUDY: COLOR VARIATION**

Sample substrates of seasoned, weathered, and historic material with 1" labeled sample treatment stripes separated by ½" clean wood. Sample treatments applied in three layers. Test set to run from December 19, 2014 to April 1, 2015, with observational analysis and Munsell color matching to be used before and after. Intended to compare variability of color within the treatment samples as well as the comparison of change with time.

### **5.4.1 INTERIOR**

Interior exposure, set near a north facing window in New York City. Seasoned, weathered, and historic timber treated with samples of (i) raw persimmon juice, kakishibu powder dissolved in water-(ii) pure, (iii) 25% dilution, (iv) 50% dilution; (v) copper naphthenate control, and (vi) an untreated control. Secondary set for interior exposure to test for color

variability of treatments on seasoned wood treated with raw persimmon juice, kakishibu in water with no dilution, 10% dilute, 20% dilute, 30%, 40%, 50%, 60%, 70%, 80%, and 90% dilute.

#### **5.4.2 EXTERIOR**

Exterior exposure, set in a north facing, partially shaded exposure, New York City (second story fire escape, shielded from metal with coating and zip tied using inert plastic).

Seasoned, weathered, and historic timber; treated with samples of (i) raw persimmon juice, kakishibu in water-(ii) pure, (iii) 25% dilution, (iv) 50% dilution; (v) copper naphthenate, (vi) untreated control.

### **5.5 VISUAL STUDY: WEATHERING**

Sample substrates of seasoned, weathered, and historic material with 1" labeled sample treatment stripes separated by ½" or more of clean wood. Sample treatments applied in three layers. Test set to run from December 19, 2014 to April 1, 2015. Exterior exposure, set in a north facing, partially shaded exposure, New York City (second story fire escape, shielded from metal with coating and zip tied using inert plastic)

Seasoned, weathered, and historic timber; treated with samples of (i) raw persimmon juice, kakishibu in water-(ii) pure, (iii) 25% dilution, (iv) 50% dilution; (v) copper naphthenate, (vi) untreated control.

Comparative observational analysis of the effects of short term weathering on all treatments and substrate combination conducted in a before/after format. Typical temperature ranges, maximum temperature, minimum temperature, and precipitation events recorded. Photo documentation of samples taken directly after treatment, in exterior mounting location, and after dismount and drying.

## **5.6 VISUAL STUDY: IRON OXIDE REACTION**

Visual study of the reaction time and stability of persimmon tannin in raw form and as kakishibu with iron oxide on Cor-Ten. Samples were isolated with tape and applied in one heavy coat. Reaction time taken at initial exposure to tannins and observations noted. Observations noted again at six weeks after treatment.

# CHAPTER 6: RESULTS AND ANALYSIS

## 6.1 CONTACT ANGLE & SURFACE ABSORPTION

Each of the coating face pairs were evaluated for contact angle to inform the hydrophobic or hydrophilic nature of the surface treatment, and then timed in comparison to an evaporative control to determine surface absorption through the treatment. As the mechanism for kakishibu’s water resistance is unknown, approximate contact angle and surface absorption tests were performed to shed light on the treatment’s ability to form a barrier. As seen in the following table, both of the persimmon coatings showed significantly higher approximated contact angles than the control sample.

		Contact Angle	
<i>Radial</i>	K <sub>p</sub>	90	
	K <sub>25</sub>	80	
	K <sub>50</sub>	60	
	Raw	80	
	Untreated	40	
<i>Transverse (End Grain)</i>	K <sub>p</sub>	120	
	Raw	140	
	Untreated	90	

In analyzing the different dilutions of Kakishibu, one can see that the dilution directly effects the contact angle. It is unknown why the radial and end grain contact angles values differ so significantly across the board. Initially it was assumed due to the difference in the size of the droplet used (1mL on transverse, 2mL on radial), however in reviewing the video

documentation, the formation of the droplet shows the contact angle difference throughout its formation on all samples.

The timed results of the surface absorption test are shown in the following chart as time elapsed, time deviance from the evaporative control, and as a percentage of the absorption time compared to the evaporative control.

		Time elapsed (min)	Time from control (min)	% from Control
<i>Radial</i>	K <sub>p</sub>	171	7	4.27%
	K <sub>25</sub>	166	2	1.22%
	K <sub>50</sub>	81	-83	-50.61%
	Raw Juice	158	-6	-3.66%
	Untreated	66	-98	-59.76%
	Evaporative Control	164		
<i>Transverse (End Grain)</i>	K <sub>p</sub>	81	6	8.00%
	Raw	67	-8	-10.67%
	Untreated	1	-74	-98.67%
	Evaporative Control	75		

While all but one of the tested surface treatments fell within 11% of the evaporative control, the kakishibu exceeded the evaporative control time in radial and transverse surface tests. The only exception being the 50% dilute kakishibu which failed through the coating and emerged as visible moisture outside of the treatment area. This failure is consistent with the manner in which an excess of carrier can rendering the tannins unable to link together to form a waterproof/ hydrophobic barrier.<sup>155</sup> From this, we can understand that kakishibu, in very much the same way as other tannins are used to create hydrophobic conditions in hide

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<sup>155</sup> Cannas, "Tannins: Fascinating, but Sometimes Dangerous Molecules".

tanning, create a film as a barrier that is effected by the dilution and only superficially penetrates the surface.

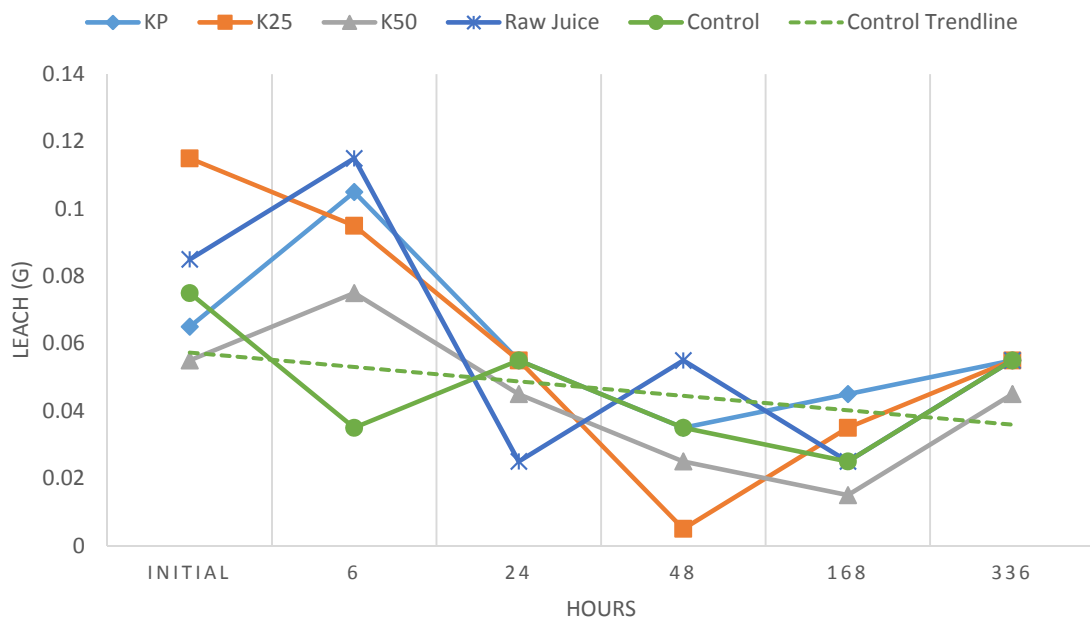
## 6.2 LEACHING TEST

To measure the permanence of the treatments, samples were saturated with water and immersed for 14 days. The water was drained off daily and particulates measured by filtration from leach water collected at 6 hours, 24 hours, 48 hours, 7 days, and 14 days. After the 14 day cycle, the samples were dried and weighed to calculate treatment loss.

Permanence is measured as the percent of treatment remaining in the sample after the leaching cycle.

### 6.2.1 RESULTS

The filtered leach water was measured to produce the following graphic showing the behavior of the leach in comparison to the control. Copper Napthenate was redacted from this graphic due to how its initial leach measurement was over 500% of the other treatment leach.



The control for this test, as untreated wood samples, are leaching out amounts of natural extractive as well as impurities in the water caught within the filter. The extractive content being leached out of the wood may be an explanation for the leach values for the persimmon treatments that dip below the control. If the persimmon is acting as a barrier at the surface of the wood, it would not only be preventing or partially preventing water from penetrating the wood, but also preventing solubilization of natural extractives.

From the comparison from the initial weight measurements of the treated blocks in comparison to the weight measurements of the blocks after the leaching cycle, percent permanence is able to be derived.

<b><i>Treatment</i></b>	<b>Treatment (g)</b>	<b>Leach (g)</b>	<b>Permanence (%)</b>
<i>CuN</i>	4.17	1.63	60.91
<i>Kp</i>	1.22	0.52	57.38
<i>K25</i>	0.96	0.54	43.75
<i>K50</i>	0.74	0.44	40.54
<i>Raw Juice</i>	1.83	1.22	33.33

As seen in the full table of results<sup>156</sup> several weights were calculated as a weight gain rather than loss from the sample. As this did not occur with the copper naphthenate control, but did with the untreated control, it is probable that there is excess moisture trapped in the wood behind the water resistant coating from the persimmon treatments. For verification that these numbers were within an acceptable limit, an error factor was determined by examining the leach to initial weight ratio of the control sample. All the gain values were within the range exhibited by the control, and all but one (SR2) fell below the average error factor of 0.0493.

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<sup>156</sup> See Appendix



### 6.2.2 CONCERNS

While conducting this test, there were several concerns about the components and process of the test including a variability of weight measure due to mechanical issues, the variability of the filter weight, and the effect of the waterproofing ability of the persimmon products on the filter paper.

The concerns over variability in weight is due to both the type of scale used and the possible inclusion of residual moisture in the wood and paper products despite air drying. Initially, a scale that allows for one hundredth of a measurement (0.00) was used to measure weights; however, after air pressure continuously destabilized the readings, samples were reweighed using a scale that only has up to a tenth of a measurement (0.0). As a single entity, this would be a slight margin of error (approx.  $\pm 0.05$  or 5%), the addition of the six values could be up to  $\pm 0.3$  (30%) variance in the total weight of the collective samples. The issue was later resolved and all paper products and final weights were recorded using the more precise scale with no variability issues.

The unknown variability of filter weight initially posed an issue to understanding the data. Out of the box on the day of testing, the product measured 0.26g but after running the filter through as a control with deionized water through Büchner funnel and oven drying, the filter paper measured 0.35g. A second and third control filter was checked and had a dry weight of 0.3g and 0.31g, wet thoroughly and without running through the Büchner system was oven dried and resulted in a weight of 0.33g. These Whatman filters, according to the material data (available in Appendix C) have a grammage of  $97\text{g/m}^2$ , which at a radius of 0.035m, the filters are supposed to weigh approximately 0.37g. In the end, the numbers 0.26g,

0.305g, and 0.35g were singled out and the final numbers were run back through using each of the filter weights by subtracting six (6) times the filter weight variable (the total number of filters used) from the known total leach and filter weight, and comparing to the actual weight leached to determine in which range would produce comparable numbers. The results can be seen in Appendix A: Tabulated Results: Leaching Analysis for Filter Weight, where the average value of 0.305g resulted in no extraneous or negative values. As such, this value was used in calculating the preservative leaching and retention as seen in the rest of Appendix A.

The waterproofing ability of astringent persimmon products is well known and used traditionally and in modern paper and textile work as a waterproofing agent for cloth, paper, and other fibrous products, the waterproofing activity of the solutions was tested on wood to show various levels of contact angle (see [6.1 Contact Angle](#)) however the effect of the solution on the filter paper may have been the cause of several issues in the leaching process. The 24 hour soak of raw juice and *kaki* solutions resulted in the solutions having a more viscous, and in the case of the raw juice, cloudy gel appearance of the solution. The fluids were much harder to pull through the paper on the Büchner, resulting in 20 minutes to four hours with standing solution above the paper (initial tests were completed in less than a minute for all solutions).

### **6.3 SOIL BLOCK TEST**

The modified soil block cultures were aimed at reviewing the ability of the persimmon treatments to resist fungal attack. The sample jars were incubated for 12 weeks to promote fungal growth on the samples. Upon disassembly of the jars, it was discovered that there was

noticeable patterns of mold growth on the samples, but after drying and weighing, the final mass loss data was inconclusive.

The lack of correlating numerical data from the fungal analysis is not a complete loss, due to the observational value of analyzing where mold growth was occurring. 100% of the controls had noticeable mold growth, while the kakishibu and the copper naphthenate control deterred mold completely, and only 22% of raw juice treated samples exhibited growth.

While the accelerated testing may have proven to be a factor in the inconclusive mass loss data, the more probable option is an ongoing issue with maintaining relative humidity. Mold growth requires >80% relative humidity, whereas fungal growth requires >97% relative humidity or with free water present.<sup>157</sup> Fluctuations in temperature and humidity did occur, and the humidity recorded inside the jars was consistently lower than 90%, despite standing water.

## 6.4 VISUAL STUDY: COLOR VARIATION

Guidance Document G of the AWWPA handbook defines surface applied wood preservative finish testing nomenclature.<sup>158</sup> From this, the observations of the color palette are as follows: raw juice is clear—meaning “any product, water borne or solvent borne, that does not obscure or alter the aesthetic qualities (color, texture, etc.) of the substrate upon application and drying”—and kakishibu ranges from semi-transparent—“Any product, water borne or solvent borne, that alters a substrate’s color but does not hide or obscure the grain pattern or surface texture that may be present”—to solid-stain—“Any product, water borne or

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<sup>157</sup> Aganost, "Wood Decay, Fungi, Stain, and Mold."27

<sup>158</sup> American Wood Protection Association, *A.W.P.A. Book of Standards*.573

solvent borne, that changes a substrate's color and hides the grain pattern, but does not obscure the surface texture." The definition of toned finish—essentially a semi-transparent that is greatly affected by the color of the substrate itself—in application to kakishibu and raw juice needs further study on sample palettes of wood. The increasing dilutions of kakishibu tested show a similar red-brown color, but less opacity. The initial and final Munsell values and approximate RGB colors are available in Appendix C.

#### **6.4.1 INTERIOR EXPOSURE CHANGE**

After the four months of exposure to interior conditions and indirect sunlight, kakishibu developed a richer and darker tone and the raw juice produced a glossy slightly darker film on the sample area. The same darkening occurred with the lower dilutions of the kakishibu. All coatings stayed within their initial category as described by the nomenclature of Guidance Document G.

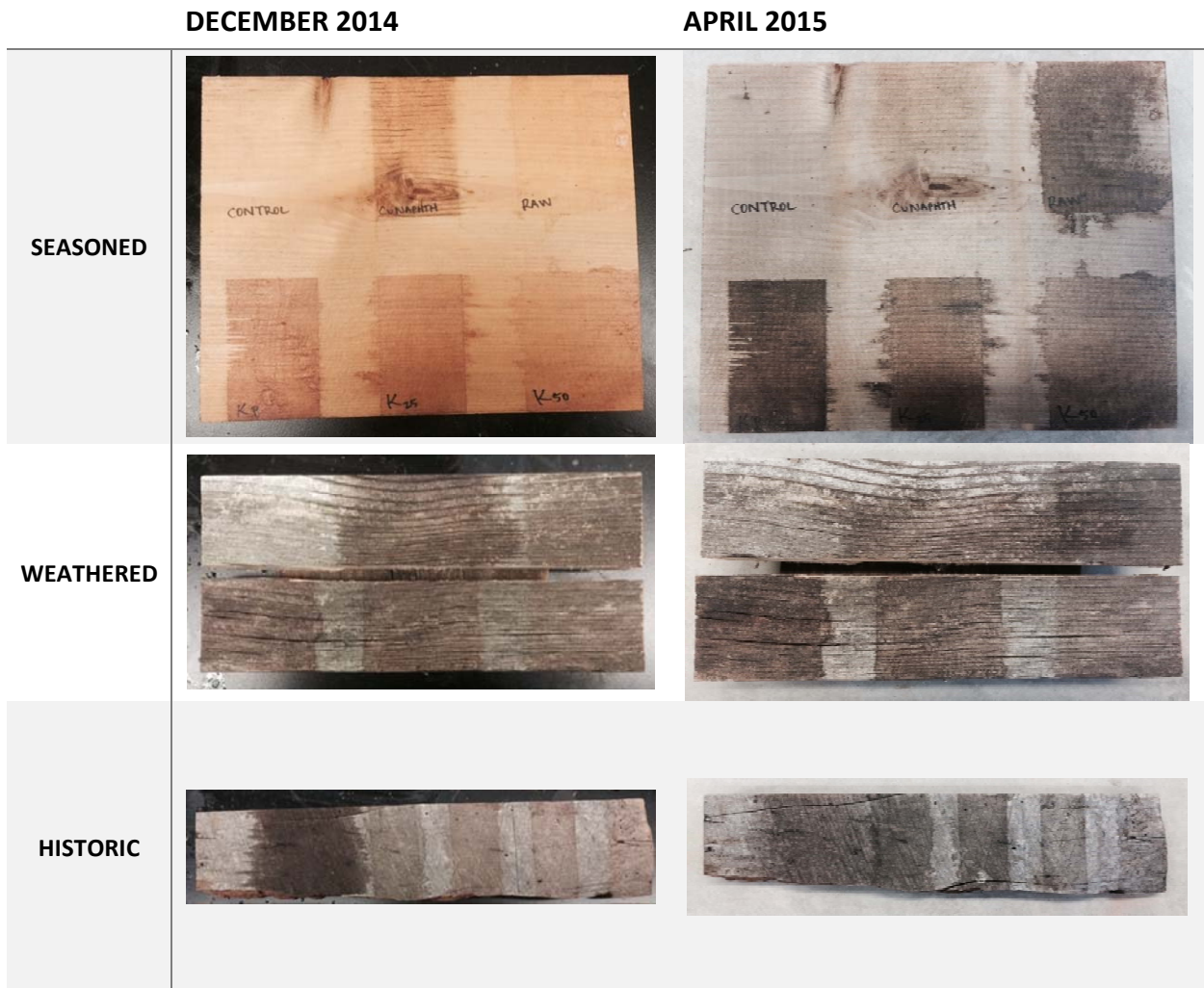
#### **6.4.2 EXTERIOR EXPOSURE CHANGE**

After the exterior exposure, the wooden substrate had significantly bleached whereas the kakishibu darkened and the initial red tones noted in the color assay diminished, leaving dark brownish black coated areas. The raw juice treated area significantly darkened and became semitransparent.

### **6.5 VISUAL STUDY: WEATHERING**

The short term weathering test was part of the exterior exposure test for color variation, but also looked at the visibility of the treatment area after several months exposed

to the elements. The following graphic shows the before and after images of all three substrates with their treatment coatings.



**Table 6.** Comparison of visual change in color and opacity with exterior exposure. Treatments on each piece: [first row, left to right] control, copper naphthenate, raw juice; [second row, left to right] Kakishibu .05, .0375, .025. Historic is same left to right

As noted in the previous section, the color change of the treatments was much more drastic than anticipated in some cases. The seasoned material accentuates the change of color tone from the bleaching of the red tones of the wood and the loss of the red tones from the treatments. It is quite obvious that the treatments are not light stable, however they all seem to retain a significant amount of visible treatment area. The kakishibu is barely effected,

however there is a fair amount of loss on the raw juice treatment area of the seasoned sample. The weathered and historic samples seem unchanged—that is other than the loss of the CuN visible treatment on the weathered and its takeover of the surrounding sample areas on the historic sample.

## **6.6 VISUAL STUDY: IRON OXIDE REACTION**

Due to research leaning towards tannins being the main bioactive mechanism of persimmon juice as a treatment, a brief test to assess the reaction of persimmon with iron oxides was conducted. The hypothesis that a reaction similar to that of the creation of a film—possibly a conversion layer as seen with tannic acid treatment—was successful. The marked off areas of the stock sample of patinated Cor-Ten was treated with kakishibu and raw persimmon juice, and within five minutes there was a considerable visual change to the treated areas, resulting in a film that appeared to be similar to the conversion layer produced during tannic acid treatment.

The results were revisited after several weeks and the treated kakishibu area was easily abraded away—brushed away with minimal force using only a gloved hand—while the raw juice had produced a mechanically stable film. This result was duplicated—in error—by B. Whitehead in his uses of kakishibu on wooden roof shingles with iron nails. He documented a purple stain radiating from the rusted nails after treating the wood.<sup>159</sup>

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<sup>159</sup> Personal communication, B. Whitehead. 12/2014

## CHAPTER 7: CONCLUSIONS & RECOMMENDATIONS

In review of the literature, we know that there is historic precedent for its use with fibrous materials, and we have a long list of preservative identified chemicals from the plant matter itself. The contact angle and surface absorption test showed a water resistance with full evaporation of the test drop and no absorption for the kakishibu samples, and within 10 percent of the evaporative control for the raw juice, and the leaching test showed undiluted kakishibu to have comparable preservative permanence to CuN. The soil block culture, despite the inconclusive mass loss data, has valuable qualitative data on surface mold growth deterrence in the kakishibu samples. The color variation tests showed a surprising result of darkening over time for the treatments; a feature that has been confirmed by textiles artists working with kakishibu as a dye. This darkening is startlingly apparent in the raw juice when exposed to sunlight in exterior testing, however otherwise the treatment areas retain their visibility throughout the weathering process. And finally, the exploration of persimmon's reaction with iron oxide, a common element in preservation, shows considerably fast visible change and a glossy well adhered film from the raw juice. Conclusively, the analyzed forms of persimmon from these tests show significant promise as a possible wood preservative.

While this treatment may not be seen as suitable for industrial preservation, where the hope is to reduce or remove the need for maintenance or retreatment. Instead, it would be well suited as a preservative for curated historic objects and buildings where sustainability—as both an ecological concept and the ability to extend the lifetime of a curated object—and object health are paramount.

## 7.1 RECCOMENDATIONS

Further study derived from this information should diverge into two paths: a deeper investigation into persimmon as a wood preservative, and a broader spectrum of research into the confluence of traditional materials and methods, food science, pharmacology, and chemotaxonomy.

My personal inability to translate Japanese and the often minimal international availability of certain literature do count as a limitation of research; however, it also leaves room for the bibliography of this work to be expanded by oral tradition and written works from the Asiatic region itself. This can also be said about the research from the broadened field of aligning traditional medicine and cultural practice, where it is possible a sustainable conservation solution exists in most indigenous herbalist practices.

The deeper investigation into persimmon will require the extensive testing suggested by the AWPA for new preservative compounds—at least the tests available to surface applied preservatives. This should also include an in depth study of persimmon’s interaction with other building materials such as stone, lime, cement, brick, etc. where there may be an issue with iron oxide destabilization or discoloration.

While the preliminary results of persimmon’s ability merits further research from the promising findings alone, the pre-existing global distribution of Japanese persimmon as well as its increasing annual yield show a favorable environment for long term research. The global distribution of this product (and its relative ease of transport) would be able to compensate for a major issue with naturally occurring decay resistant woods—proximity to market and



available supply.<sup>160</sup> In addition, there is potential for significant financial incentive due to the ability to produce the analyzed treatments from unmarketable or “trash” crop. Because the extractives can be produced from damaged, misshapen, and aesthetically unappealing persimmon—all factors that limit the marketable agricultural yield of orchard production—there is no risk of produce sale prices destabilizing the resource availability. The development of a stable persimmon treatment from astringent, but mature persimmons, increases overall revenue for orchards and would be manageable for long term agricultural waste diversion, and incredibly cost effective due to the annual yield constituting as a rapidly renewable resource. The closest viable bioalternative would be derived from timber extractives from wood, roots, and bark that require substantial damage or felling of the tree. Fruit is a yield product where a percentage is lost due to damage or physical deformities--neither of which affect the astringent product.

So, one can conclusively say that persimmons are much, *much* more than a standard produce; and instead it seems that the persimmon could be one of the next steps in producing a sustainable future.

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<sup>160</sup> American Wood Protection Association, *A.W.P.A. Book of Standards*.15-1

## FURTHER READING

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Mallavadhani, U.V., AK Panda, YR Rad. "Pharmacology and Chemotaxonomy of *Diospyros*." *Phytochemistry* 49(4) (1998): 901-951

Collective tables listing the traditional uses, chemical component research, and pharmacology of the *Diospyros* genus.

Zenjirou, Tamura & Morimoto Takashi. "宮本常一とあるいた昭和の日本." Rural Culture Association (23) 2012 (Japanese)

Traditional persimmon lacquering technique and interview with a lacquerer.

## GLOSSARY

**Hoshigaki** : traditional hand processed persimmon that is air dried and develops a sugary coating. Originally used as a preservation process; commonly used in festival celebrations.

**Kakinoha-zushi** (Kaki-no-ha-sushi) : sushi wrapped in persimmon leaf

**Mokume dashi** : lacquering process that colors the wood red but allows for the grain to show through the nuri

**Nuri** : Traditional lacquering process

**Shibu-sumi-nuri** (shibu-ji) : lacquer treatment using persimmon tannin mixed with charcoal.

Commonly seen on lacquerware.

**Shou-sugi-ban** (yakasugi) : carbonized Japanese cedar (*Cryptomeria japonica*) used for fire-resistance. Traditional technique of charring sugi boards to heat treat the wood and increase its durability and fire resistance. This process is currently popular for its aesthetic and has been reverse engineered to create a modern acetylation process for the siding and decking market.<sup>161</sup>

**Sugi** : common name for Japanese cedar and cypress,

**Sumi** : charcoal, lamp black

**Urushi** : Traditional plant derived lacquer

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<sup>161</sup>R. Rowell, "Acetylation of Wood: Journey From Analytical Technique to Commercial Reality," *Forest Products Journal* 56, no. 9 (2006). & T Kilian, "Shou-Sugi-Ban," *Wood Design & Building* 2014.

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## APPENDIX A: TABULATED LEACHING ANALYSIS

### LEACHING ANALYSIS FOR FILTER WEIGHT

Substrate	Coating	W1	W2	WT (W1-W2)	W3	WL (W2-W3)	Corrected	Σ WL	Σ W2	Σ WT	Total Leach & Filter weight	Filter weights & Leach Calc.*				Σ WL / Σ WT	% collected in leach water		
												0.26	0.278	0.305	0.35				
Seasoned	Kakishibu 0.05g/mL	2.52	2.84	0.32	2.76	0.08	0.08	0.52	20.14	1.22	2.19	0.63	0.52	0.36	0.09	0.426	29.51%		
Seasoned		2.69	2.88	0.19	2.9	-0.02	0												
Weathered		2.76	2.95	0.19	2.9	0.05	0.05												
Weathered		2.65	2.87	0.22	2.73	0.14	0.14												
Historic		4	4.1	0.1	3.92	0.18	0.18												
Historic		4.3	4.5	0.2	4.43	0.07	0.07												
Seasoned	Kakishibu 0.0375g/mL	2.49	2.57	0.08	2.51	0.06	0.06	0.54	24.74	0.96	2.19	0.63	0.52	0.36	0.09	0.514	0.563	33.56%	37.50%
Seasoned		2.31	2.79	0.48	2.65	0.14	0.14												
Weathered		5.08	5.26	0.18	5.07	0.19	0.19												
Weathered		4.9	5.02	0.12	5.08	-0.06	0												
Historic		4.2	4.25	0.05	4.1	0.15	0.15												
Historic		4.8	4.85	0.05	4.89	-0.04	0												
Seasoned	Kakishibu 0.025g/mL	2.7	2.98	0.28	2.89	0.09	0.09	0.44	23.21	0.74	2.09	0.53	0.42	0.26	-0.01	0.595	35.14%		
Seasoned		2.46	2.63	0.17	2.56	0.07	0.07												
Weathered		4.73	4.89	0.16	4.88	0.01	0.01												
Weathered		4.18	4.21	0.03	4.26	-0.05	0												
Historic		4.2	4.25	0.05	4.13	0.12	0.12												
Historic		4.2	4.25	0.05	4.1	0.15	0.15												
Seasoned	Raw <i>kaki</i> Juice	2.39	2.43	0.04	2.25	0.18	0.18	1.22	22.94	1.83	2.19	0.63	0.52	0.36	0.09	0.667	19.67%		
Seasoned		2.52	2.97	0.45	3.13	-0.16	0												
Weathered		4.43	4.8	0.37	4.84	-0.04	0												
Weathered		2.47	2.94	0.47	2.63	0.31	0.31												
Historic		4.7	5	0.3	4.56	0.44	0.44												
Historic		4.6	4.8	0.2	4.51	0.29	0.29												

Substrate	Coating	W1	W2	WT (W1-W2)	W3	WL (W2-W3)	Corrected	Σ WL	Σ W2	Σ WT	Total Leach & Filter weight	Filter weights & Leach Calc.*				Σ WL / Σ WT	% collected in leach water
												0.26	0.278	0.305	0.35		
Seasoned	Copper Naphth.	2.89	3.78	0.89	3.72	0.06	0.06	1.63	27.45	4.17	2.65	1.09	0.98	0.82	0.55	0.391	19.66%
Seasoned		2.42	2.75	0.33	2.45	0.3	0.3										
Weathered		4.68	5.5	0.82	4.93	0.57	0.57										
Weathered		4.49	5.82	1.33	5.13	0.69	0.69										
Historic		4	4.5	0.5	4.49	0.01	0.01										
Historic		4.8	5.1	0.3	5.12	-0.02	0										
Seasoned	None	2.28	2.31	0.03	2.3	0.01	0.01	0.29	23.37	0.44	2.11	0.55	0.44	0.28	0.01		
Seasoned		2.3	2.38	0.08	2.41	-0.03	0										
Weathered		5.25	5.3	0.05	5.7	-0.4	0										
Weathered		4.6	4.68	0.08	5.31	-0.63	0										
Historic		4.3	4.5	0.2	4.29	0.21	0.21										
Historic		4.2	4.2	0	4.13	0.07	0.07										

**Bad** value greater than Σ WL

\*established by subtracting six (6) times the filter weight variable (the total number of filters used) from the known total leach and filter weight and comparing to the actual weight leached

**RECORDED FILTER LEACH**

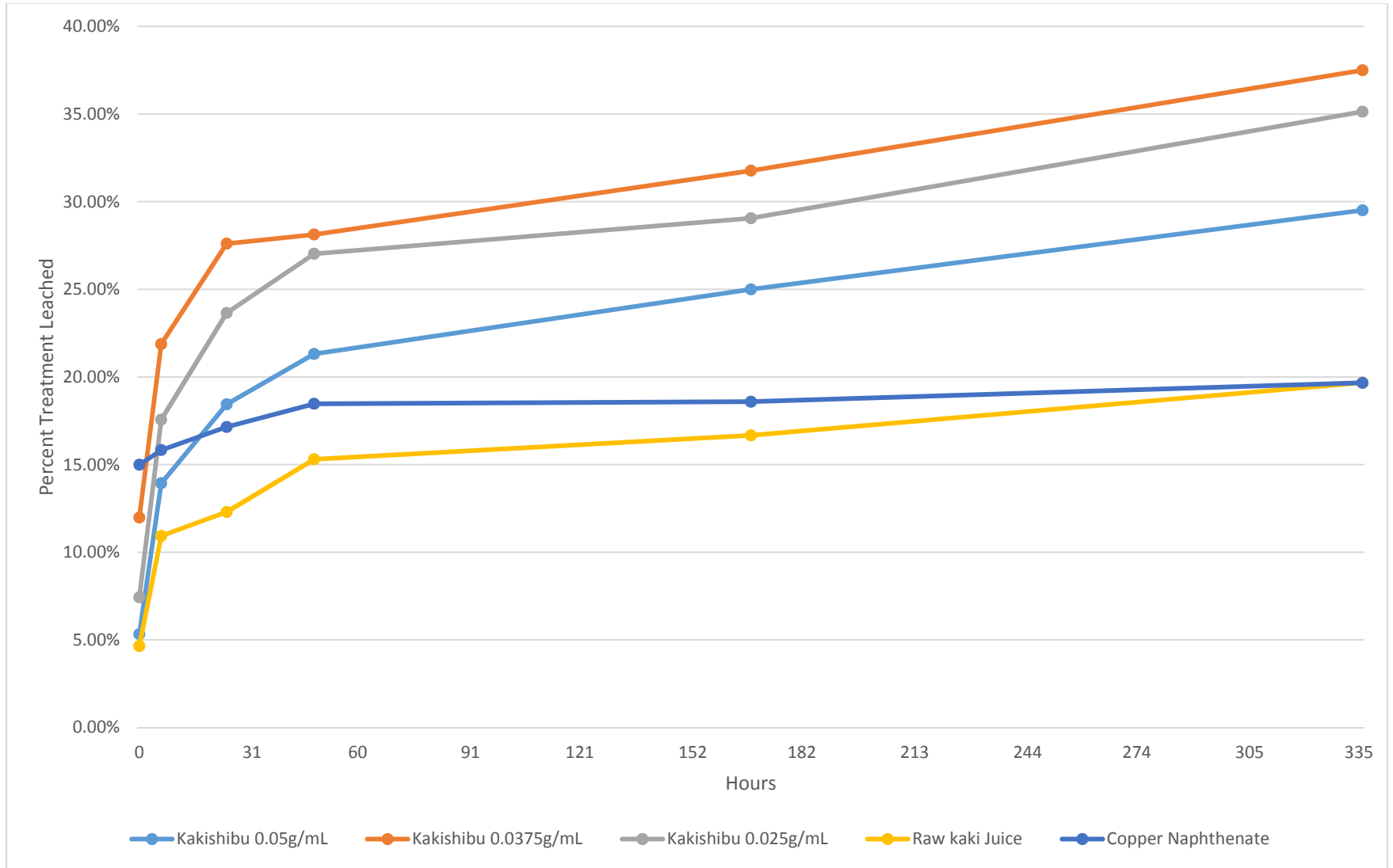
#	Substrate	Treatment	W1	W2	WT (W1-W2)	Σ W2	Σ WT	Filters	Time (hrs)																							
									0	6	24	48	168	336																		
SK <sub>p</sub> 1	Seasoned	Kakishibu 0.05g/mL	2.52	2.84	0.32	20.14	1.22	0.305	Recorded weight	0.37	0.41	0.36	0.34	0.35	0.36																	
SK <sub>p</sub> 2			2.69	2.88	0.19																											
WK <sub>p</sub> 1	Weathered		2.76	2.95	0.19																											
WK <sub>p</sub> 2			2.65	2.87	0.22																											
HK <sub>p</sub> 1	Historic		4	4.1	0.1																											
HK <sub>p</sub> 2			4.3	4.5	0.2																											
SK <sub>25</sub> 1	Seasoned		Kakishibu 0.0375g/mL	2.49	2.57											0.08	24.74	0.96	0.305	Recorded weight	0.42	0.4	0.36	0.31	0.34	0.36						
SK <sub>25</sub> 2				2.31	2.79											0.48																
WK <sub>25</sub> 1	Weathered	5.08		5.26	0.18																											
WK <sub>25</sub> 2		4.9		5.02	0.12																											
HK <sub>25</sub> 1	Historic	4.2		4.25	0.05																											
HK <sub>25</sub> 2		4.8		4.85	0.05																											
SK <sub>50</sub> 1	Seasoned	Kakishibu 0.025g/mL		2.7	2.98	0.28	23.21	0.74	0.305	Recorded weight	0.36	0.38	0.35	0.33	0.32	0.35																
SK <sub>50</sub> 2				2.46	2.63	0.17																										
WK <sub>50</sub> 1	Weathered		4.73	4.89	0.16																											
WK <sub>50</sub> 2			4.18	4.21	0.03																											
HK <sub>50</sub> 1	Historic		4.2	4.25	0.05																											
HK <sub>50</sub> 2			4.2	4.25	0.05																											
SR1	Seasoned		Raw <i>kaki</i> Juice	2.39	2.43	0.04											22.94	1.83	0.305	Recorded weight	0.39	0.42	0.33	0.36	0.33	0.36						
SR2				2.52	2.97	0.45																										
WR1	Weathered	4.43		4.8	0.37																											
WR2		2.47		2.94	0.47																											
HR1	Historic	4.7		5	0.3																											
HR2		4.6		4.8	0.2																											
SCN1	Seasoned	Copper Naphthenate		2.89	3.78	0.89	27.45	4.17	7.17	Recorded weight	8.1	0.34	0.36	0.36	0.31	0.35																
SCN2				2.42	2.75	0.33																										
WCN1	Weathered		4.68	5.5	0.82																											
WCN2			4.49	5.82	1.33																											
HCN1	Historic		4	4.5	0.5	0.305			Combined total weight collected								0.625	0.66	0.715	0.77	0.775	0.82										
HCN2			4.8	5.1	0.3																											
SC1	Seasoned		None	2.28	2.31	0.03																	23.37	0.44	0.305	Recorded weight	0.38	0.34	0.36	0.34	0.33	0.36
SC2				2.3	2.38	0.08																										
WC1	Weathered	5.25		5.3	0.05																											
WC2		4.6		4.68	0.08																											
HC1	Historic	4.3		4.5	0.2																											
HC2		4.2		4.2	0																											
									Combined total weight collected	0.075	0.11	0.165	0.2	0.225	0.28																	
									Percent leached	17.05%	25.00%	37.50%	45.45%	51.14%	63.64%																	

**PERMANENCE**

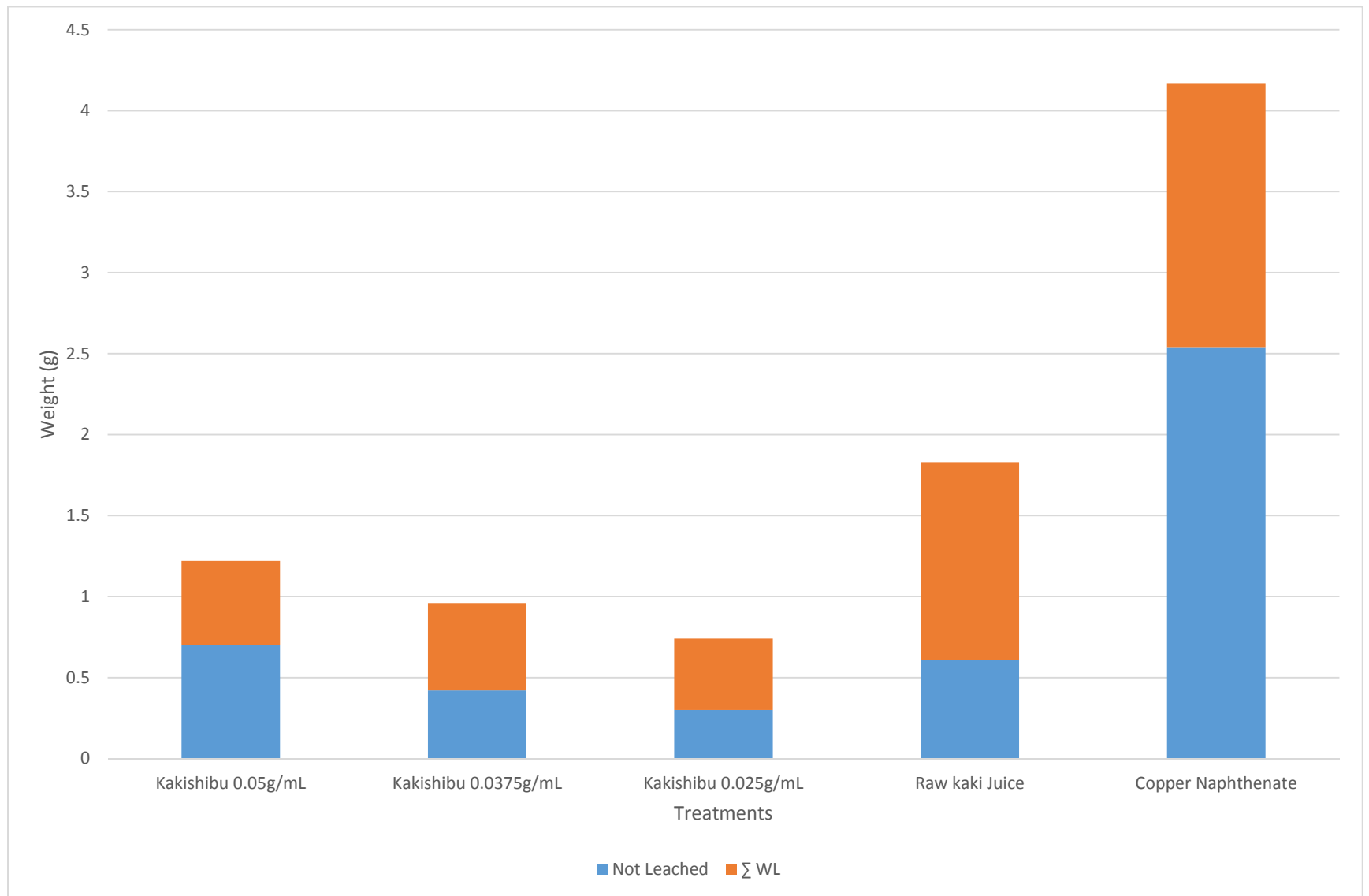
#	Substrate	Treatment	W1	W2	WT (W1-W2)	Σ W2	Σ WT	W3	L	WL (W2-W3)	Σ W3	Σ WL	% Leached (Σ WL / Σ WT)	Permanence (1-% Leached)	Error factor								
SK <sub>p</sub> 1	Seasoned	Kakishibu 0.05g/mL	2.52	2.84	0.32	20.14	1.22	2.76	0.08	0.08	19.64	0.52	42.62%	57.38%	0.007434944								
SK <sub>p</sub> 2			2.69	2.88	0.19			2.9	-0.02	0													
WK <sub>p</sub> 1	Weathered		2.76	2.95	0.19			2.9	0.05	0.05													
WK <sub>p</sub> 2			2.65	2.87	0.22			2.73	0.14	0.14													
HK <sub>p</sub> 1	Historic		4	4.1	0.1			3.92	0.18	0.18													
HK <sub>p</sub> 2			4.3	4.5	0.2			4.43	0.07	0.07													
SK <sub>25</sub> 1	Seasoned		Kakishibu 0.0375g/mL	2.49	2.57			0.08	24.74	0.96						2.51	0.06	0.06	24.3	0.54	56.25%	43.75%	0.012244898
SK <sub>25</sub> 2				2.31	2.79			0.48								2.65	0.14	0.14					
WK <sub>25</sub> 1	Weathered	5.08		5.26	0.18	5.07	0.19	0.19															
WK <sub>25</sub> 2		4.9		5.02	0.12	5.08	-0.06	0															
HK <sub>25</sub> 1	Historic	4.2		4.25	0.05	4.1	0.15	0.15															
HK <sub>25</sub> 2		4.8		4.85	0.05	4.89	-0.04	0															
SK <sub>50</sub> 1	Seasoned	Kakishibu 0.025g/mL		2.7	2.98	0.28	23.21	0.74			2.89	0.09	0.09	22.82	0.44	59.46%	40.54%	0.011961722					
SK <sub>50</sub> 2				2.46	2.63	0.17					2.56	0.07	0.07										
WK <sub>50</sub> 1	Weathered		4.73	4.89	0.16	4.88			0.01	0.01													
WK <sub>50</sub> 2			4.18	4.21	0.03	4.26			-0.05	0													
HK <sub>50</sub> 1	Historic		4.2	4.25	0.05	4.13			0.12	0.12													
HK <sub>50</sub> 2			4.2	4.25	0.05	4.1			0.15	0.15													
SR1	Seasoned		Raw <i>kaki</i> Juice	2.39	2.43	0.04			22.94	1.83	2.25	0.18	0.18						21.92	1.22	66.67%	33.33%	0.063492063
SR2				2.52	2.97	0.45					3.13	-0.16	0										
WR1	Weathered	4.43		4.8	0.37	4.84	-0.04	0															
WR2		2.47		2.94	0.47	2.63	0.31	0.31															
HR1	Historic	4.7		5	0.3	4.56	0.44	0.44															
HR2		4.6		4.8	0.2	4.51	0.29	0.29															
SCN1	Seasoned	Copper Naphthenate		2.89	3.78	0.89	27.45	4.17			3.72	0.06	0.06	25.84	1.63	39.09%	60.91%	0.004166667					
SCN2				2.42	2.75	0.33					2.45	0.3	0.3										
WCN1	Weathered		4.68	5.5	0.82	4.93			0.57	0.57													
WCN2			4.49	5.82	1.33	5.13			0.69	0.69													
HCN1	Historic		4	4.5	0.5	4.49			0.01	0.01													
HCN2			4.8	5.1	0.3	5.12			-0.02	0													
SC1	Seasoned		None	2.28	2.31	0.03			23.37	0.44	2.3	0.01											
SC2				2.3	2.38	0.08					2.41	-0.03											
WC1	Weathered	5.25		5.3	0.05	5.7	-0.4																
WC2		4.6		4.68	0.08	5.31	-0.63																
HC1	Historic	4.3		4.5	0.2	4.29	0.21																
HC2		4.2		4.2	0	4.13	0.07																

Control error factor (<|L|/W1>) 0.0493

## PERCENT TREATMENT LEACHED OVER TEST CYCLE



## TREATMENT WEIGHTS WITH LEACHED AND UNLEACHED TREATMENT



## APPENDIX B: TABULATED SOIL CULTURE

### JAR OBSERVATIONS

#	Test Group	Jar	Substrate	Coating	Jar observation
1	A1	A1S	Seasoned	Kakishibu 0.05g/mL	N/A
2	A1	A1S	Seasoned	Raw <i>kaki</i> Juice	N/A
3	A1	A1S	Seasoned	Copper Naphthenate	N/A
4	A1	A1S	Seasoned	None	Blue stain and mold present
5	A1	A1W	Weathered	Kakishibu 0.05g/mL	N/A
6	A1	A1W	Weathered	Raw <i>kaki</i> Juice	N/A
7	A1	A1W	Weathered	Copper Naphthenate	N/A
8	A1	A1W	Weathered	None	Blue stain and mold present
9	A1	A1H	Historic	Kakishibu 0.05g/mL	N/A
10	A1	A1H	Historic	Raw <i>kaki</i> Juice	N/A
11	A1	A1H	Historic	Copper Naphthenate	N/A
12	A1	A1H	Historic	None	Blue stain and white mold
13	A2	A2S	Seasoned	Kakishibu 0.05g/mL	N/A
14	A2	A2S	Seasoned	Raw <i>kaki</i> Juice	N/A
15	A2	A2S	Seasoned	Copper Naphthenate	N/A
16	A2	A2S	Seasoned	None	Mold
17	A2	A2W	Weathered	Kakishibu 0.05g/mL	N/A
18	A2	A2W	Weathered	Raw <i>kaki</i> Juice	N/A
19	A2	A2W	Weathered	Copper Naphthenate	N/A
20	A2	A2W	Weathered	None	Mold
21	A2	A2H	Historic	Kakishibu 0.05g/mL	N/A
22	A2	A2H	Historic	Raw <i>kaki</i> Juice	N/A
23	A2	A2H	Historic	Copper Naphthenate	N/A
24	A2	A2H	Historic	None	Mold and tan and black fuzzy coating
25	B1	B1S	Seasoned	Kakishibu 0.0375g/mL	N/A
26	B1	B1S	Seasoned	Raw <i>kaki</i> Juice	N/A
27	B1	B1S	Seasoned	Copper Naphthenate	N/A
28	B1	B1S	Seasoned	None	Blue stain and mold
29	B1	B1W	Weathered	Kakishibu 0.0375g/mL	N/A
30	B1	B1W	Weathered	Raw <i>kaki</i> Juice	Black mold
31	B1	B1W	Weathered	Copper Naphthenate	N/A
32	B1	B1W	Weathered	None	Fuzzy black
33	B1	B1H	Historic	Kakishibu 0.0375g/mL	N/A

#	Test Group	Jar	Substrate	Coating	Jar observation
34	B1	B1H	Historic	Raw <i>kaki</i> Juice	N/A
35	B1	B1H	Historic	Copper Naphthenate	N/A
36	B1	B1H	Historic	None	White mold
37	B2	B2S	Seasoned	Kakishibu 0.0375g/mL	N/A
38	B2	B2S	Seasoned	Raw <i>kaki</i> Juice	N/A
39	B2	B2S	Seasoned	Copper Naphthenate	N/A
40	B2	B2S	Seasoned	None	Mold
41	B2	B2W	Weathered	Kakishibu 0.0375g/mL	N/A
42	B2	B2W	Weathered	Raw <i>kaki</i> Juice	N/A
43	B2	B2W	Weathered	Copper Naphthenate	N/A
44	B2	B2W	Weathered	None	Fuzzy black
45	B2	B2H	Historic	Kakishibu 0.0375g/mL	N/A
46	B2	B2H	Historic	Raw <i>kaki</i> Juice	N/A
47	B2	B2H	Historic	Copper Naphthenate	N/A
48	B2	B2H	Historic	None	White mold
49	C1	C1S	Seasoned	Kakishibu 0.025g/mL	N/A
50	C1	C1S	Seasoned	Raw <i>kaki</i> Juice	N/A
51	C1	C1S	Seasoned	Copper Naphthenate	N/A
52	C1	C1S	Seasoned	None	Mold, minimal
53	C1	C1W	Weathered	Kakishibu 0.025g/mL	N/A
54	C1	C1W	Weathered	Raw <i>kaki</i> Juice	N/A
55	C1	C1W	Weathered	Copper Naphthenate	N/A
56	C1	C1W	Weathered	None	Blue stain and mold
57	C1	C1H	Historic	Kakishibu 0.025g/mL	N/A
58	C1	C1H	Historic	Raw <i>kaki</i> Juice	N/A
59	C1	C1H	Historic	Copper Naphthenate	N/A
60	C1	C1H	Historic	None	Blue stain mold black gunk
61	C2	C2S	Seasoned	Kakishibu 0.025g/mL	N/A
62	C2	C2S	Seasoned	Raw <i>kaki</i> Juice	N/A
63	C2	C2S	Seasoned	Copper Naphthenate	N/A
64	C2	C2S	Seasoned	None	Blue stain mold
65	C2	C2W	Weathered	Kakishibu 0.025g/mL	N/A
66	C2	C2W	Weathered	Raw <i>kaki</i> Juice	N/A
67	C2	C2W	Weathered	Copper Naphthenate	N/A
68	C2	C2W	Weathered	None	blue stain mold
69	C2	C2H	Historic	Kakishibu 0.025g/mL	N/A
70	C2	C2H	Historic	Raw <i>kaki</i> Juice	White mold
71	C2	C2H	Historic	Copper Naphthenate	N/A
72	C2	C2H	Historic	None	White mold, super fuzzy



## LOSS ANALYSIS BY JAR

#	Group	Jar	Substrate	Coating	W <sub>1</sub>	W <sub>2</sub>	W <sub>C</sub> (W <sub>1</sub> -W <sub>2</sub> )	W <sub>3</sub>	W <sub>L</sub> (W <sub>2</sub> -W <sub>3</sub> )	% Loss
1	A1	A1S	Seasoned	Kakishibu 0.05g/mL	2.48	2.62	0.14	2.44	0.18	6.87%
2	A1	A1S	Seasoned	Raw <i>kaki</i> Juice	2.71	3.2	0.49	2.88	0.32	10.00%
3	A1	A1S	Seasoned	Copper Naphthenate	2.41	2.64	0.23	2.51	0.13	4.92%
4	A1	A1S	Seasoned	None	2.7	2.79	0.09	2.71	0.08	2.87%
5	A1	A1W	Weathered	Kakishibu 0.05g/mL	3.72	3.92	0.2	3.76	0.16	4.08%
6	A1	A1W	Weathered	Raw <i>kaki</i> Juice	2.62	2.9	0.28	2.61	0.29	10.00%
7	A1	A1W	Weathered	Copper Naphthenate	3.74	4.12	0.38	3.73	0.39	9.47%
8	A1	A1W	Weathered	None	3.4	3.48	0.08	3.36	0.12	3.45%
9	A1	A1H	Historic	Kakishibu 0.05g/mL	3.8	3.9	0.1	3.66	0.24	6.15%
10	A1	A1H	Historic	Raw <i>kaki</i> Juice	4.7	4.8	0.1	4.46	0.34	7.08%
11	A1	A1H	Historic	Copper Naphthenate	4	4.4	0.4	4.21	0.19	4.32%
12	A1	A1H	Historic	None	4.4	4.5	0.1	4.21	0.29	6.44%
13	A2	A2S	Seasoned	Kakishibu 0.05g/mL	2.38	2.56	0.18	2.42	0.14	5.47%
14	A2	A2S	Seasoned	Raw <i>kaki</i> Juice	2.54	2.68	0.14	2.42	0.26	9.70%
15	A2	A2S	Seasoned	Copper Naphthenate	2.53	2.82	0.29	2.66	0.16	5.67%
16	A2	A2S	Seasoned	None	2.73	2.73	0	2.65	0.08	2.93%
17	A2	A2W	Weathered	Kakishibu 0.05g/mL	2.72	3.11	0.39	2.96	0.15	4.82%
18	A2	A2W	Weathered	Raw <i>kaki</i> Juice	2.77	3.1	0.33	2.8	0.3	9.68%
19	A2	A2W	Weathered	Copper Naphthenate	2.37	3.62	1.25	3.37	0.25	6.91%
20	A2	A2W	Weathered	None	2.7	2.73	0.03	2.56	0.17	6.23%
21	A2	A2H	Historic	Kakishibu 0.05g/mL	4.4	4.5	0.1	4.24	0.26	5.78%
22	A2	A2H	Historic	Raw <i>kaki</i> Juice	4.2	4.3	0.1	4.12	0.18	4.19%
23	A2	A2H	Historic	Copper Naphthenate	4.1	4.3	0.2	4.23	0.07	1.63%
24	A2	A2H	Historic	None	5	5.1	0.1	4.81	0.29	5.69%
25	B1	B1S	Seasoned	Kakishibu 0.0375g/mL	2.42	2.56	0.14	2.41	0.15	5.86%
26	B1	B1S	Seasoned	Raw <i>kaki</i> Juice	2.51	2.93	0.42	2.67	0.26	8.87%
27	B1	B1S	Seasoned	Copper Naphthenate	2.57	2.81	0.24	2.64	0.17	6.05%
28	B1	B1S	Seasoned	None	2.82	2.87	0.05	2.77	0.1	3.48%
29	B1	B1W	Weathered	Kakishibu 0.0375g/mL	2.53	2.9	0.37	2.78	0.12	4.14%
30	B1	B1W	Weathered	Raw <i>kaki</i> Juice	2.46	3.02	0.56	2.6	0.42	13.91%

#	Group	Jar	Substrate	Coating	W <sub>1</sub>	W <sub>2</sub>	W <sub>C</sub> (W <sub>1</sub> -W <sub>2</sub> )	W <sub>3</sub>	W <sub>L</sub> (W <sub>2</sub> -W <sub>3</sub> )	% Loss
31	B1	B1W	Weathered	Copper Naphthenate	3.4	4.54	1.14	3.94	0.6	13.22%
32	B1	B1W	Weathered	None	2.62	2.63	0.01	2.52	0.11	4.18%
33	B1	B1H	Historic	Kakishibu 0.0375g/mL	3.9	3.95	0.05	3.67	0.28	7.09%
34	B1	B1H	Historic	Raw <i>kaki</i> Juice	4.3	4.5	0.2	4.2	0.3	6.67%
35	B1	B1H	Historic	Copper Naphthenate	4.2	4.5	0.3	4.33	0.17	3.78%
36	B1	B1H	Historic	None	4.2	4.3	0.1	4.01	0.29	6.74%
37	B2	B2S	Seasoned	Kakishibu 0.0375g/mL	2.83	3.05	0.22	2.92	0.13	4.26%
38	B2	B2S	Seasoned	Raw <i>kaki</i> Juice	2.48	2.65	0.17	2.45	0.2	7.55%
39	B2	B2S	Seasoned	Copper Naphthenate	2.54	2.86	0.32	2.71	0.15	5.24%
40	B2	B2S	Seasoned	None	2.62	2.71	0.09	2.64	0.07	2.58%
41	B2	B2W	Weathered	Kakishibu 0.0375g/mL	2.7	2.82	0.12	2.66	0.16	5.67%
42	B2	B2W	Weathered	Raw <i>kaki</i> Juice	2.51	2.92	0.41	2.63	0.29	9.93%
43	B2	B2W	Weathered	Copper Naphthenate	4	4.31	0.31	3.84	0.47	10.90%
44	B2	B2W	Weathered	None	2.61	2.73	0.12	2.64	0.09	3.30%
45	B2	B2H	Historic	Kakishibu 0.0375g/mL	4	5	1	3.78	1.22	24.40%
46	B2	B2H	Historic	Raw <i>kaki</i> Juice	4.9	5.1	0.2	4.74	0.36	7.06%
47	B2	B2H	Historic	Copper Naphthenate	3.8	4.1	0.3	4	0.1	2.44%
48	B2	B2H	Historic	None	4	4.1	0.1	3.8	0.3	7.32%
49	C1	C1S	Seasoned	Kakishibu 0.025g/mL	2.84	3.1	0.26	2.93	0.17	5.48%
50	C1	C1S	Seasoned	Raw <i>kaki</i> Juice	2.49	2.68	0.19	2.54	0.14	5.22%
51	C1	C1S	Seasoned	Copper Naphthenate	2.4	2.73	0.33	2.51	0.22	8.06%
52	C1	C1S	Seasoned	None	2.8	2.85	0.05	2.75	0.1	3.51%
53	C1	C1W	Weathered	Kakishibu 0.025g/mL	2.5	2.59	0.09	2.49	0.1	3.86%
54	C1	C1W	Weathered	Raw <i>kaki</i> Juice	2.73	3.35	0.62	3	0.35	10.45%
55	C1	C1W	Weathered	Copper Naphthenate	3.89	4.54	0.65	4.12	0.42	9.25%
56	C1	C1W	Weathered	None	2.8	2.94	0.14	2.85	0.09	3.06%
57	C1	C1H	Historic	Kakishibu 0.025g/mL	3.85	3.9	0.05	3.65	0.25	6.41%
58	C1	C1H	Historic	Raw <i>kaki</i> Juice	4.1	4.4	0.3	4.15	0.25	5.68%
59	C1	C1H	Historic	Copper Naphthenate	4.4	5.2	0.8	4.94	0.26	5.00%
60	C1	C1H	Historic	None	4.4	4.5	0.1	4	0.5	11.11%
61	C2	C2S	Seasoned	Kakishibu 0.025g/mL	2.5	2.64	0.14	2.53	0.11	4.17%
62	C2	C2S	Seasoned	Raw <i>kaki</i> Juice	2.32	2.48	0.16	2.31	0.17	6.85%
63	C2	C2S	Seasoned	Copper Naphthenate	3.05	3.65	0.6	3.34	0.31	8.49%

#	Group	Jar	Substrate	Coating	W <sub>1</sub>	W <sub>2</sub>	W <sub>C</sub> (W <sub>1</sub> -W <sub>2</sub> )	W <sub>3</sub>	W <sub>L</sub> (W <sub>2</sub> -W <sub>3</sub> )	% Loss
64	C2	C2S	Seasoned	None	2.4	2.42	0.02	2.3	0.12	4.96%
65	C2	C2W	Weathered	Kakishibu 0.025g/mL	2.44	2.6	0.16	2.53	0.07	2.69%
66	C2	C2W	Weathered	Raw <i>kaki</i> Juice	2.72	2.94	0.22	2.57	0.37	12.59%
67	C2	C2W	Weathered	Copper Naphthenate	4.83	5.31	0.48	4.4	0.91	17.14%
68	C2	C2W	Weathered	None	2.68	2.68	0	2.51	0.17	6.34%
69	C2	C2H	Historic	Kakishibu 0.025g/mL	4.55	4.6	0.05	4.35	0.25	5.43%
70	C2	C2H	Historic	Raw <i>kaki</i> Juice	3.9	4.3	0.4	3.77	0.53	12.33%
71	C2	C2H	Historic	Copper Naphthenate	4.8	5.1	0.3	4.94	0.16	3.14%
72	C2	C2H	Historic	None	4.3	4.4	0.1	4.09	0.31	7.05%

# APPENDIX C: VISUAL STUDIES

## COLOR VARIATION: MUNSELL COMPARISON

Substrate	Treatment	Munsell Color Before	Interior After	Exterior After
<i>Seasoned</i>	None	2.5Y 8.5/4	10YR 7/6	2.5Y 7/2
<i>Seasoned</i>	CuN	2.5Y 5/6	2.5Y 6/6	2.5Y 7/4
<i>Seasoned</i>	Raw	2.5Y 8.5/6	10YR 6/6	2.5Y 4/2
<i>Seasoned</i>	Kp	2.5YR 4/8	5YR 3/6	5YR 2/2
<i>Seasoned</i>	K <sub>25</sub>	5YR 5/6	7.5YR 5/6	7.5YR 3/2
<i>Seasoned</i>	K <sub>50</sub>	5YR 5/7	7.5YR 5/6	2.5Y 4/2
<i>Weathered</i>	None	5Y 8/1	5Y 5/1	5Y 8/1
<i>Weathered</i>	CuN	5Y 2/2	2.5Y 3/2	2.5Y 6/2
<i>Weathered</i>	Raw	10YR 5/2	10YR 3/1	2.5Y 5/2
<i>Weathered</i>	Kp	5YR 2/2	5YR 2/2	5YR 3/1
<i>Weathered</i>	K <sub>25</sub>	7.5YR 3/2	7.5YR 3/2	10YR 4/2
<i>Weathered</i>	K <sub>50</sub>	7.5YR 4/2	7.5YR 4/2	10YR 4/2
<i>Historic</i>	None	10YR 8/1	10YR 8/1	10YR 6/1
<i>Historic</i>	CuN	10YR 2/2	10YR 6/2	10YR 4/1
<i>Historic</i>	Raw	10YR 7/2	10YR 7/2	10YR 3/1
<i>Historic</i>	Kp	2.5YR 3/4	2.5YR 3/4	10YR 3/2
<i>Historic</i>	K <sub>25</sub>	5YR 4/2	5YR 4/2	10YR 4/2
<i>Historic</i>	K <sub>50</sub>	5YR 4/4	5YR 4/4	10YR 4/2

# APPENDIX D: MATERIAL DATA

## HISTORIC MATERIAL

- Sourced from a loft floor board in a barn on the Jones property in Owego, NY.
- Age of the sample is approximately 150 years based on known construction on the property.
- Observations: sample shows signs of weathering, rust staining, and prior insect infestation. Gray surface patina with rich orange and red toned wood. Frass collected from insect markings, which are irregular direction tunnels filled with powder frass. Piece is severely cracked (now in two pieces) in one location with major and minor cracking throughout. Large arc mill saw markings on both sides.
- Dimensions: 1 3/16" x 9" x 13" at widest points. Tangential planes with some remaining exterior curvature from tree.
- Frass sample, powder texture, and tunnel diameter (1.5-2mm) indicate powderpost beetle of *Lyctus sp.* as likely former infestation.
- Identification: hardwood, large number of narrow rays in two widths with semi ring to diffuse pore structure; small solitary pores with several chain type structures. Microscopic analysis of cross section identified intervessel pitting, tangential rays, and spiral thickening, leading the piece to be identified as Maple.

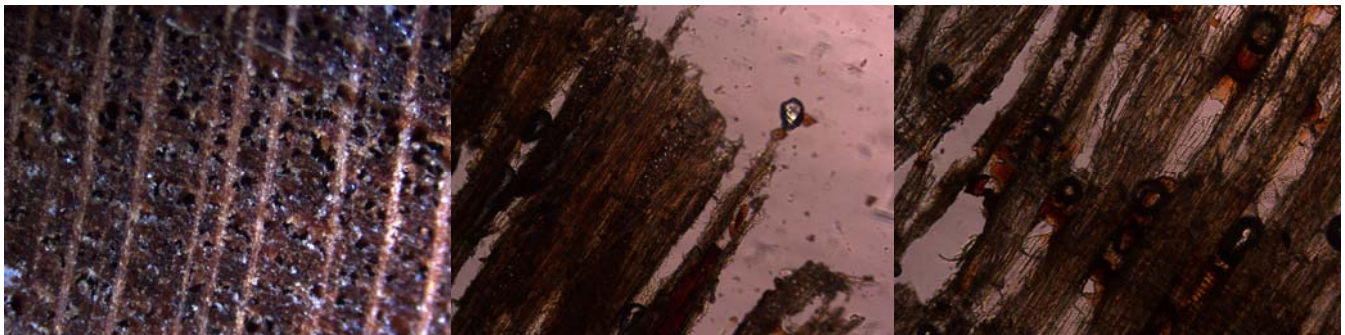


Figure 6. Identification features: (i) diffuse pore structure, (ii) intervessel pitting, (iii) spiral thickening

## ACTIVE FUNGAL SAMPLE

The infected wood source was provided by Lori Arnold, of Arnold Wood Conservation LLC. The felled oak log was located at the bottom of a carpenter's wood pile in the Greater Philadelphia Area of Pennsylvania. It is noted that the log has gone through thermal cycling and seasonal change, possibly more than once, and was stored cold in an uncontrolled environment. Fruiting bodies and bioactivity were emergent upon a return to a heat and moisture controlled environment.

- Observations: Severely deteriorated wood sample with multiple fungal and insect identifiers. Live insects are apparent, as is soil inclusion. Wood deterioration and channeling is filled with loose and compacted frass, deteriorated wood, and unidentified organic matter. Wood is sectionally bleached white and soft to the touch and crumbles



upon pressure; intact wood is also apparent. Bark is loose and has severe deterioration along interior edge. Fruiting bodies of multiple fungal types are evident; typified by an orange-brown leathery crust or groups of irregular, hemi-circular white/off-white/gray plates measuring 2-5cm in length.

- Identification: Fungal samples were identified through Lori Arnold's observations and the use of the *Eumycota* taxon division of the Encyclopedia of Life at EOL.org. The wood destroying fungi are mainly of the *Dikarya* subkingdom of *Eumycota*, with phyla of *Basidiomycota* and in the *Polyporaceae* family. Brown leathery crust is typical fruiting body

of *Poria incrassata*, or dry rot. White/gray plate shaped fungus is typical of *Trametes sp.*, more than likely *Trametes pubescens*, a form of white rot. Other possible genii include *Poronidulus sp.* and *Coriolus sp.* While the white rot may be the cause of the soft deterioration of the wood, it is possible that other forms of soft rot in the Ascomycota phyla or the Deuteromycota variant of the Dikarya—which are asexual—could be extant and causing the structural deterioration of the wood. Frass samples, which were heavily granular, reflect termite infestation and possible Anobiidae—deathwatch beetle—presence. Due to the severe deterioration and organic matter covering the sample, powdery frass was unidentifiable and distinct tunneling or exit markings could not be identified.

- Sample collection: A mixture of loose organic matter, fruiting bodies, frass, and deteriorated wood was collected for use as the fungal component in the wood block tests.



# WHATMAN NO.2 FILTERS

[USA Home](#) WMA1002070 - Whatman® qualitative filter paper, Grade 2

**SIGMA-ALDRICH**

WMA1002070 ALDRICH

## Whatman® qualitative filter paper, Grade 2

circles, diam. 70 mm, pack of 100

Synonym: Whatman filter, Whatman paper, Z340206, paper filter

[MDS](#) [SIMILAR PRODUCTS](#)



### Properties

Related Categories	<a href="#">Filtration Supplies, Labware, Paper Filters, Qualitative</a>
material	circles
mfr. no.	Whatman Article No., Z3413956 (US reference) Whatman, 1002-070
packaging	pack of 100
limit	0.29 psi wet burst
	240 sec/100 mL speed (Herzberg)
diam.	70 mm
thickness	190 µm
ash	±0.06%
pore size	8 µm (Particle retention)
basis weight	97 g/m <sup>2</sup>
	<a href="#">Show Fewer Properties</a>

### Description

#### General description

These cellulose filters are used in qualitative analytical techniques to determine and identify materials. Prepleated qualitative filters are also available, which give improved flow rate and increased loading capacity compared to equivalent flat filters.

#### Grade 2: 8 µm, (medium flow filter paper)

Slightly more retentive than Grade 1 with a corresponding increase in filtration time (i.e., slightly slower filtration speed). More absorbent than Grade 1. In addition to general filtration in the 8 µm particle size range, the extra absorbency is utilized, for example, to hold soil nutrient in plant growth trials. Also used for monitoring specific contaminants in the atmosphere and in soil testing.

#### Other Notes

Field of Use : For internal research use only. Products are not intended for diagnostic use or resale.

#### Legal information

Whatman is a registered trademark of GE Healthcare

### Price and Availability

SKU-Pack Size	Availability	Price (USD)	Quantity
WMA1002070	Available to ship on 02/18/15 - FROM	13.00	<input type="text" value="0"/>

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## Safety Information

Safety information for this product is unavailable at this time.

# COPPER GREEN™ BROWN WOOD PRESERVATIVE



## MATERIAL SAFETY DATA SHEET

Effective Date : February 28, 2014

### SECTION 1 – PRODUCT IDENTIFICATION

**Material Name:** COPPER-GREEN® & COPPER-GREEN® Brown Wood Preservative

**Product Description:** Dark green or brown liquid for applying to wood to prevent various wood destroying insect infestation, water damage, wood rot, fungus & mold.

**Manufacturer:** Green Products Company, 810 Market Avenue, Richmond, CA 94801 Tel : (510) 235 9667

**EPA Registration No:** 66591-1 California EPA Establishment No. 066591-CA-01

EPA Registration permits are renewed annually expiring December 31 of each year.

**EMERGENCY No:** 1-800-535-5053

**Product Use:** A wood preservative that contains copper for preventing various types of wood damage.

**Product Restrictions:** Do not use on any material other than wood. Should not be applied to food or feed surfaces. FOR EXTERIOR USE ONLY (See approved label on product)

### SECTION 2 – HAZARD(S) IDENTIFICATION

Hazards to humans and domestic animals

May be fatal if swallowed. Causes eye and skin irritation. Do not get in eyes, on skin or on clothing. Do not breathe vapor or spray mist. Wear a mask or pesticide respirator jointly approved by the Mine Safety and Health Administration and the National Institute for Occupational Safety and Health.

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**MATERIAL SAFETY DATA SHEET**

- Irritant (Inhalation, skin and eyes)

CAUTION – Application of this product may produce a strong, lingering, unpleasant odor. Vapors may cause headache, nausea and respiratory tract irritation.

HAZARDOUS MATERIALS IDENTIFICATION SYSTEM (HMIS): HEALTH-1  
FLAMMABILITY-0 REACTIVITY-0

(Product not regulated by the Department of Transportation.)

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a National Pollution Discharge Elimination System (NPDES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA.

**SECTION 3 - COMPOSITION/INFORMATION ON INGREDIENTS**

PRIVATE INGREDIENT	CAS NO.	TLV	PEL	Percentage of Product
Copper Naphthenate	1338-02-9	5	Not Available	10.0%
Process Oil	64742-58-1	Not Available	Not Available	45-55%
Mineral Spirits	64742-88-7		100ppm	30-40%
	525mg/m3			

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## MATERIAL SAFETY DATA SHEET

PRIVATE Boiling Point	For product	315-380 Deg F
Vapor Pressure	For product	20 mm Hg @ 68.00 Deg F
Specific Vapor Density	AIR = 1	4.9
Specific Gravity	H2O=1	.92
Percent Volatile		25%-35%
Evaporation Rate	Slower than ether	
Weight per Gal., Lbs.	7.10	
V.O.C.	For product	343 gm/ltr

### SECTION 4 - FIRST-AID MEASURES

**IF INHALED:** Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably by mouth-to-mouth, if possible. Call a poison control center or doctor for further treatment advice.

**IF ON SKIN OR CLOTHING:** Take off contaminated clothing. Rinse skin immediately with plenty of water for 15-20 minutes. Call a poison control center or doctor for further treatment advice.

**IF IN EYES:** Hold eye open and rinse slowly and gently with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye. Call a poison control center or doctor for treatment advice.

**IF SWALLOWED:** Immediately call a poison control center or doctor for treatment advice. Do not induce vomiting unless instructed to do so by a poison control center or doctor. Do not give any liquid to the person. Do not give anything by mouth to an unconscious person.

Have the product container or label with you when calling a poison control center or doctor or going for treatment. In case of medical questions, emergencies or accidents involving this product call INFOTRAC at (800) 535-5053.

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## MATERIAL SAFETY DATA SHEET

NOTE TO PHYSICIAN: Contains petroleum distillates – vomiting may cause aspiration pneumonia.

### SECTION 5 - FIRE-FIGHTING MEASURES

FLASHPOINT: 150-250 Deg F

EXPLOSIVE LIMIT (PRODUCT): None

FLAMMABLE LIMIT IN AIR % BY VOLUME: None

EXTINGUISHING MEDIA: Foam, CO<sub>2</sub>, dry chemical.

SPECIAL FIREFIGHTING PROCEDURES: Self-contained breathing unit. Avoid spreading with water spray.

UNUSUAL FIRE AND EXPLOSION HAZARDS: Vapors in empty drum can explode if ignited.

### SECTION 6 - ACCIDENTAL RELEASE MEASURES

Do not use, pour, spill, or store near heat or open flame. Use only with adequate ventilation. Close container when not in use.

If product has been spilled or is leaking, remove the source of the spill or leak. Recover free liquid. Spread absorbent, then pick up and place in D.O.T. waste containers. Then, where applicable, wash area with detergent and water.

### SECTION 7 - HANDLING AND STORAGE

Store in a secure, well-ventilated area, protected from extreme temperatures. Store in original container only. Do not contaminate water, food or feed by storage or disposal.

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## MATERIAL SAFETY DATA SHEET

DO NOT GET ON ANY MATERIAL OTHER THAN WOOD.

### SECTION 8 - EXPOSURE CONTROLS/PERSONAL PROTECTION

THRESHOLD LIMIT VALUE (TLV): 500 ppm

RESPIRATORY PROTECTION: NIOSH approved air mask in contained area.

EYE PROTECTION: Goggles.

PROTECTIVE GLOVES: Neoprene.

OTHER PROTECTIVE EQUIPMENT: Not generally required. But safety clothes would be recommended.

### SECTION 9 - PHYSICAL AND CHEMICAL PROPERTIES

Do not use, pour, spill, or store near heat or open flame. Use only with adequate ventilation. Close container when not in use. Soluble in mineral spirits or organic solvents.

### SECTION 10 - STABILITY AND REACTIVITY

STABILITY: Stable      CONDITIONS TO AVOID: None.

INCOMPATIBILITY (Materials to Avoid): Strong oxidizing agents.

HAZARDOUS DECOMPOSITION: Incomplete combustion may release carbon monoxide.

HAZARDOUS POLYMERIZATION: Will not occur.

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## MATERIAL SAFETY DATA SHEET

### SECTION 11 - TOXICOLOGICAL INFORMATION

#### Toxicological Data on Ingredients:

Mineral Spirits: ACUTE ORAL (LD50): >1710 mg/kg [Rat]

ACUTE DERMAL (LD50): >1710 mg/kg [Rabbit]

Copper Naphthanate: ACUTE ORAL (LD50): 294 mg/kg [Rat]

278.859 mg/kg [Mouse]

Routes of Entry: Absorbed through skin. Eye contact. Inhalation. Ingestion.

#### Toxicity to Animals:

Copper Naphthanate: ACUTE ORAL (LD50): 278.859 mg/kg [Mouse]

Mineral Spirits: ACUTE DERMAL: 1710 mg/kg [Rabbit]

Special Remarks on Toxicity to Animals: Mineral Spirits: Inhalation (mist) Lethal Dose/Conc: .648.774 mg/m<sup>3</sup>/4H [Rat]

Chronic Effects on Humans: Contains material which may cause damage to the following organs: blood, kidneys, the nervous system, and peripheral nervous system.

#### Special Remarks on other Toxic Effects on Humans:

Slightly hazardous in case of skin contact (irritant, permeator) of ingestion and of inhalation.

#### Acute Potential Health Effects:

Skin: It may cause skin irritation.

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## MATERIAL SAFETY DATA SHEET

**Eyes:** Contact may cause eye irritation. Contact may also cause conjunctivitis. Vapors may be irritating to the eyes.

**Inhalation:** This product may cause upper respiratory tract irritation. Excessive inhalation of this products vapors, which contains mineral spirits may affect behavior/central nervous system and cause dizziness, drowsiness, somnolence, convulsions, tremors, lightheadedness, passing-out, impairment of short term memory, loss of coordination and judgment, personality changes (withdrawal, irritability), fatigue, sleep disturbances, headache, giddiness, stupor, unconsciousness, followed by coma. It can also affect the nerves supplying internal organs (automatic nerves) and/or peripheral nerves to the legs and arms (weakness, "pins and needles"). It can also cause nausea and vomiting, chest pain, difficulty breathing. It may also affect the liver and kidneys.

**Ingestion:** Slightly toxic. Ingestion of copper salts may produce vomiting, metallic taste, headache, cold sweats, shock, jaundice, swollen liver, kidney damage, CNS depression, and death from CNS depression, or delayed death from kidney or liver failure. Whether such serious side effects occur following copper naphthenate ingestion is unknown.

**Chronic Potential Health Effects:**

**Ingestion:** Prolonged or repeated ingestion may cause anemia.

**Skin:** Prolonged or repeated skin contact may cause drying or cracking of the skin (defatting), dermatitis, irritation, skin ulcers or pruritic eczema.

**Inhalation:** Repeated or prolonged inhalation can affect behavior/central nervous system with symptoms to that of acute inhalation. It may also cause kidney damage and affect the blood (normocytic anemia).

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## **MATERIAL SAFETY DATA SHEET**

### **SECTION 12 – ECOLOGICAL INFORMATION**

Ecotoxicity: This product is toxic to aquatic invertebrates, shrimps, and oysters/clams. Avoid contamination to water bodies. Pesticides wastes are toxic. Improper disposal of excess pesticides, spray mixture, or rinsate is a violation of federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste Representative at the nearest EPA Regional Office for guidance.

### **SECTION 13 – DISPOSAL CONSIDERATIONS**

Nonrefillable container. Do not reuse or refill this container. Triple rinse container (or equivalent) promptly after emptying. Water is not effective for removing residues of this product and will create a rinsate that needs to be disposed of. Use of mineral spirits for triple rinsing the container is effective and will allow the rinsate to be used as part of the application mixture. Triple rinse as follows: Empty the remaining contents into application equipment or a mix tank. Fill the container  $\frac{1}{4}$  full with mineral spirits and recap. Shake for 10 seconds. Pour the rinsate into application equipment or a mix tank or store rinsate for later use or disposal. Drain for 10 seconds after pour begins to drip. Repeat this procedure two more times. Then offer for recycling, if available, or puncture and dispose of in a sanitary landfill, or incineration, or, if allowed by state and local ordinances, by burning. If burned, stay out of smoke.

### **SECTION 14 – TRANSPORT INFORMATION**

DOT – United States – Department of Transportation

Ground transportation only.

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## MATERIAL SAFETY DATA SHEET

### SECTION 15 – REGULATORY INFORMATION

EPA Reg. No. 66591-1

Federal and State Regulations: Copper Naphthenate SARA 313 toxic chemical notification and release reporting: Copper Naphthenate 68%

### SECTION 16 – OTHER INFORMATION

Preparation Date : November 1, 2013

Last Known Revision Date: February 28, 2014

The information accumulated herein is believed to be accurate but is not warranted to be whether originating with the company or not. Recipients are advised to confirm in advance of need that the information is current, applicable, and suitable to their circumstances.

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## KAKISHIBU PREPARATION INSTRUCTIONS

### **Kaki Shibu - Persimmon Dye**

Kaki shibu, tannin processed from the juice of unripe persimmon fruit, is a traditional natural dye that has been used for many years in Japan. One of its applications is paper, and paper treated with kaki shibu is strengthened, repels insects and is made water resistant. Such paper traditionally had three main uses: as label paper for price tags on dry goods and cloth which was to be dyed; as stencil paper; and, when also treated with oil, as a waterproof paper for making umbrellas. This product is a granular persimmon dye.

### **Instructions for Use**

The quantities given here may be adjusted, with either stronger or more dilute solutions being possible. As repeated applications are traditionally the best way to build up a darker colour, stronger solutions are not generally necessary. Unlike most other natural dyes, persimmon darkens with age, with the majority of change taking place in the first six months after dyeing; what you see after your dyeing session will change considerably. Allowing the paper to dry after each application is recommended: working outside on a sunny day will help to speed up this process.

Kaki shibu may be applied to paper either by immersing the paper in a shallow pan of the dye (more even results) or by brushing it on. Since more applications of *kaki shibu* yield darker colours you may wish to brush the dye on in specific patterns to make the most of this feature.

### **Cautions**

- \* Kaki shibu has a *very* strong odour, and though it is non-toxic you may wish to work outdoors or in a well ventilated area. It is also a strong astringent and so should be kept out of reach of children.
- \* It will react to iron products; please use non-iron containers such as enamel or stainless steel.
- \*Kaki shibu stains. If you get dye on your clothing wash it with water immediately.
- \*Re-constituted dye will only keep for short periods in the refrigerator (no more than two weeks!) so its best to make only what will be used in one dyeing session.



## **Materials**

kakishibu powder  
kozo paper  
wide brush (or a selection of widths for patterning)  
plastic sheet or tray to hold flat sheet of paper  
stainless steel pot  
wooden spoon or stirring stick  
newsprint

## **Dye preparation**

Proportions: 25g powder to 1/2 litre water

Mix the powder into cool water until dissolved. If the mixture does not dissolve completely you may need to let it sit for up to 24 hours. It will dissolve.

Alternatively, you may also heat the powder and water in a pot on a stove and simmer it gently until it is dissolved. Avoid rapid boiling. You may add a small amount of water to replace what is lost in the simmering process. A cooking pot may be used, but it's probably best to use a dedicated spoon. A stainless steel cooking spoon may be used.

## **Brushing on shibu**

Work on a plastic covered surface or a tray large enough to fit your flat piece of paper. This will allow you to catch excess dye for reuse. You may start with dry paper or you may dampen the paper either by brushing on water with a clean brush, or by 'spritzing' water onto the sheet with a spray bottle. Working on a dampened sheet will give softer edges, and if aiming for a solid colour sheet, more even results.

This is the point where you may become creative. e.g. Brush the dye on in a plaid pattern, leaving some white showing. Work on a dry sheet of paper and thoroughly dry it between applications for crisper results. Or brush a layer of kaki shibu over the whole sheet after the patterning for less contrasty results.

## **Immersing paper in shibu**

Use pure fibred papers such as kozo or gampi which have a good wet strength. Pour enough dye into a shallow tray to cover a sheet of paper. Place a single sheet in the tray and allow it to become thoroughly wet. Carefully lift the paper out using a wooden rod for support and allow the excess liquid to drip back into the pan.

### **Drying dyed paper**

Paper may be dried flat or hung on a clothesline with pegs. While hanging a wet sheet of paper is obviously tricky, the sheet will dry more quickly than one left on a flat surface. Two pairs of hands can make the job a little easier. If working on your own try lifting the paper with a wooden dowel or ruler, with some of the paper protruding beyond its edge so that it might be held to the line for pegging. Place a tray under the hanging sheet to catch excess dye for reuse.

Paper laid flat on plastic sheeting will allow the dye to pool somewhat where it comes into contact with the plastic leaving a darker pattern. This may or may not be desirable. Plain newsprint will blot excess dye, but be careful to lift the drying paper occasionally to ensure that it doesn't stick to the newsprint. Another alternative is to use a sheet of kozo paper as a blotter, allowing the accumulated dye to create a random pattern on it.