

RE-CONSERVATION OF WOOD FROM THE SEVENTEENTH-CENTURY  
SWEDISH WARSHIP THE *VASA* WITH ALKOXYSILANES:  
A RE-TREATMENT STUDY APPLYING THERMOSETTING ELASTOMERS

A Thesis

by

CARLOS CABRERA TEJEDOR

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of  
MASTER OF ARTS

December 2010

Major Subject: Anthropology

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Approved by:

Chair of Committee,	Donny L. Hamilton
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## ABSTRACT

Re-conservation of Wood from the Seventeenth-Century

Swedish Warship the *Vasa* with Alkoxysilanes:

A Re-treatment Study Applying Thermosetting Elastomers. (December 2010)

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The purpose of this study was to explore the feasibility of re-treating artifacts previously conserved by PEG impregnation with alkoxysilanes. The study tried to evaluate pros and cons of re-conserving artifacts with this type of silanes. A series of experiments were conducted focusing on small, wood samples from the *Vasa* Museum Collection, to test different re-conservation methods. Three different procedures involving alkoxysilanes were implemented in order to re-serve the samples.

The study revealed the techniques are an efficient re-conservation method in which highly satisfactory results can be achieved. The re-treated samples present minimal volumetric distortion without significant collapse or shrinkage of the wood structures. This minimal distortion is primarily produced by the transition from swollen waterlogged wood to a dry conserved wood, and not as a result of collapse or shrinkage during treatment. Due to the negligible thickness of the polymer coating (a few microns), the samples acquire physical properties extremely close to the original dry wood.

Moreover, other physiochemical properties are obtained from the consolidation with alkoxysilanes; the re-conserved wood becomes hydrophobic, chemically inert, resistant to chemical attacks (e.g., acids or bases), and resistant to ultraviolet light. These newly acquired characteristics drastically reduce the preventive conservation measures needed in museum display cabinets or during transport.

Despite the excellent results, the procedure is not reversible, thus does not comply with one of the main premises traditionally accepted in conservation. Therefore, a careful study assessing benefits and disadvantages in a case-by-case basis should be assessed by conservators, restorers, and curators before applying this method to waterlogged material culture.

## DEDICATION

The very best of making friends is neither fulfilling first sight impressions nor having long lasting friendships, but all those good times spent together.

To friendship.

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## TABLE OF CONTENTS

	Page
ABSTRACT .....	iii
DEDICATION .....	v
ACKNOWLEDGEMENTS .....	vi
TABLE OF CONTENTS .....	viii
LIST OF FIGURES.....	xi
LIST OF TABLES .....	xv
CHAPTER	
I INTRODUCTION.....	1
Preface.....	1
Brief History of the <i>Vasa</i> .....	5
The Conservation of the <i>Vasa</i> .....	19
II SILICONES AND CONSERVATION.....	36
Silicon Chemistry .....	36
Physical and Chemical Properties of Silicones .....	39
The Use of Silicones in Inorganic Material Conservation .....	40
The Use of Silicones in Organic Material Conservation.....	42
The Use of Thermosetting Resins in Material Conservation .....	45
<i>La Belle</i> Shipwreck and Texas A&M University.....	48
Silicone Oil Treatment .....	51
III OBJECTIVES AND RESEARCH PLAN .....	59
PHASE 1: <i>Vasa</i> Museum (June 2007).....	60
PHASE 2: Texas A&M University (August 2007-May 2008) .....	62
PHASE 3: <i>Vasa</i> Museum (June 2008) .....	68



CHAPTER	Page
IV	PRE-TREATMENT DOCUMENTATION ..... 69
	Sample's Measurements of the <i>Vasa</i> Research ..... 69
V	EXPERIMENT DESIGN ..... 73
	<i>Vasa</i> Research Samples' Sub-Divisions ..... 73
	Preparation for Analysis ..... 78
VI	ANALYSIS OF THE SAMPLES ..... 83
	Physical Documentation and Analysis ..... 83
	Wood Analysis ..... 92
	Wood Identification ..... 100
	Microscopic Analysis ..... 101
	Elemental Analysis ..... 102
	Compounds Analysis: Raman/FTIR ..... 110
VII	RE-CONSERVATION PROCEDURES AND RESULTS ..... 117
	First Procedure: Silicone Oil Treatment ..... 118
	Results of the First Procedure: Silicone Oil Treatment ..... 125
	Second Procedure: MTMS re-Treatment Method ..... 140
	Results of Second Procedure: MTMS re-Treatment Method ..... 143
	Third Procedure: Author's Alternative MTMS re-Treatment Method ..... 148
	Results of Third Procedure: Author's Alternative MTMS re-Treatment Method ..... 149
VIII	OVERALL EVALUATION OF THE RESULTS ..... 160
	Evaluating the Results ..... 160
	Silicone Oil Treatment ..... 162
	MTMS re-Treatment Method ..... 163
	Author's Alternative MTMS Treatment ..... 165

CHAPTER	Page
IX DISCUSSION .....	167
Waterlogged Wood Conservation .....	167
X CONCLUSIONS .....	189
GLOSSARY .....	194
REFERENCES CITED .....	200
APPENDIX .....	232
VITA .....	236

## LIST OF FIGURES

	Page
Figure 1 The <i>Vasa</i> at the hall of its Museum in Stockholm, Sweden.....	5
Figure 2 The <i>Vasa</i> being lifted to the surface on April 24, 1961 .....	15
Figure 3 The <i>Vasa</i> hull reinforced on the floating pontoon in the dry dock .....	16
Figure 4 Carl Olof Cederlund during the excavation of the <i>Vasa</i> .....	17
Figure 5 Superstructure built over the <i>Vasa</i> on the floating pontoon.....	18
Figure 6 <i>Wasavarvet</i> , <i>Vasa</i> 's temporary museum (1962-1988) .....	18
Figure 7 The <i>Vasa</i> being conserved through the automatic spraying system.....	24
Figure 8 The ship being transported to the permanent <i>Vasa</i> Museum .....	28
Figure 9 Acidic salt precipitations .....	29
Figure 10 Replacing the rusted away original bolts .....	33
Figure 11 Aqueous solution of EDMA.....	34
Figure 12 The polymerization process of silicone.....	37
Figure 13 Photo and dimensions of the waterlogged wood sample .....	69
Figure 14 Photo and dimensions of the EDMA treated wood sample .....	70
Figure 15 Photo and dimensions of the PEG treated wood sample.....	71
Figure 16 Wood samples being divided .....	73
Figure 17 Two images of the waterlogged sample (WS) .....	74
Figure 18 Two images of the EDMA sample (ES).....	76
Figure 19 Two images of the PEG sample (PS) .....	77

	Page
Figure 20 Two images of the slicing process .....	79
Figure 21 Sections of the samples .....	79
Figure 22 Spots for analysis .....	81
Figure 23 Three images of the freeze drying process.....	82
Figure 24 Munsell® Color System.....	85
Figure 25 Spatial distribution of the three axes of wood.....	87
Figure 26 Two images of the optical scanning process.....	88
Figure 27 Two images of the optical scanning process.....	89
Figure 28 3D digitalization of the six sub-samples obtained from the PEG sample .....	90
Figure 29 3D modeling software Rhinoceros® interface showing PEG sub-samples .....	91
Figure 30 The three planes of wood .....	93
Figure 31 Two different techniques of sawing lumber.....	94
Figure 32 Image from the Rhinoceros® software interface.....	95
Figure 33 Reconstructed position of waterlogged sample.....	96
Figure 34 Reconstructed position of EDMA sample.....	97
Figure 35 Reconstructed position PEG sample.....	98
Figure 36 Two microscopic photographs of wood slices .....	101
Figure 37 Two images form the EDS analysis of WS1-A2 spot.....	104
Figure 38 Example of XPS spectrum .....	106
Figure 39 Example of Raman/FTIR raw spectrum of WS sample after conservation .....	111

	Page
Figure 40 Different beakers of DI water after PEG extraction.....	119
Figure 41 Weight variation of PEG sample (PS) during PEG extraction.....	120
Figure 42 Sub-sample WS4 during dehydration process .....	121
Figure 43 Container with the polymer mixture .....	122
Figure 44 Catalysis of the samples .....	124
Figure 45 Macroscopic results of WS4 .....	126
Figure 46 ESEM micrographs of oak sample (WS4) .....	129
Figure 47 Macroscopic results of ES4.....	131
Figure 48 ESEM micrographs of pine sample (ES4) .....	134
Figure 49 Macroscopic results of PS5 .....	136
Figure 50 ESEM micrographs of pine sample (PS5).....	139
Figure 51 Weight variation of pine sub-sample (i.e. PS6) during MTMS re-treatment method .....	141
Figure 52 Beaker with used MTMS .....	142
Figure 53 Macroscopic results of PS6 .....	144
Figure 54 ESEM micrographs of the pine sample (PS6).....	147
Figure 55 Macroscopic results of ES3.....	151
Figure 56 ESEM micrographs of pine sample (ES3) .....	154
Figure 57 Three macroscopic photographs of the pine sample (PS4).....	156
Figure 58 ESEM micrographs of pine sample (PS4).....	159
Figure 59 ESEM micrograph of PEG treatment.....	170

	Page
Figure 60 ESEM micrograph of pine sample (ES) after being freeze dried.....	175
Figure 61 Two SEM micrographs of pine sample (PS4).....	180
Figure 62 SEM micrograph of pine sample (PS6).....	181

## LIST OF TABLES

	Page
Table 1	Main differences between <i>plastination</i> and silicone oil..... 52
Table 2	Proposed pre-treatment documentation..... 62
Table 3	Main processes of the proposed re-conservation treatments..... 64
Table 4	Proposed post-treatment documentation. .... 67
Table 5	Summary of the different procedures applied to the sub-samples ..... 117
Table 6	Summary of the physical characteristics of oak sample (WS4)..... 127
Table 7	Summary of the physical characteristics of pine sample (ES4) ..... 132
Table 8	Summary of the physical characteristics of pine sample (PS5) ..... 137
Table 9	Summary of the physical characteristics of pine sample (PS6) ..... 145
Table 10	Summary of the physical characteristics of pine sample (ES3) ..... 152
Table 11	Summary of the physical characteristics of pine sample (PS4) ..... 157
Table 12	Evaluated parameters and grades of the six final sub-samples ..... 161
Table 13	Measurements of oak waterlogged sample and its sub-samples before and after the different re-conservation treatments applied..... 232
Table 14	Measurements of pine EDMA sample and its sub-samples before and after the different re-conservation treatments applied..... 233
Table 15	Measurements of pine PEG sample and its sub-samples before and after the different re-conservation treatments applied..... 234

## CHAPTER I

### INTRODUCTION

#### **Preface**

A better understanding of our ancestors, their culture, traditions, and way of life can be achieved through the study of the material culture that we inherited from them. The study of these historical and cultural testimonies cannot be accomplished if this heritage is not protected from natural deterioration and decay.

“An archaeological excavation that does not conserve, destroys.” Under this premise, in all archaeological excavation it is necessary to plan and execute a series of conservation measures destined to preserve the extracted artifacts.

UNESCO (2001) acknowledged the importance of underwater cultural heritage as an integral part of the cultural heritage of humanity and a particularly important element in the history of peoples, nations, and their relations with each other concerning their common heritage. The international agreement entitled the Protection of the Underwater Cultural Heritage (UNESCO 2001) states that all excavations that do not include the knowledge, both technical and human, necessary to assure a correct conservation of the recovered artifacts are not approved.

The materials recovered from underwater excavations need extraordinary measures of manipulation and treatment from the moment of their extraction from the

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This thesis follows the style of the *Society for American Archaeology*.



seabed to their stabilization in the laboratory (Pearson 1987:105-121). Due to the special estate of preservation in which these materials are found, and due to the extreme fragility and decay that organic material presents, the selection of a suitable conservation method is necessary but extremely complex (Hoffmann 2007).

Waterlogged wood is a particularly difficult material to deal with and complex to conserve (Grattan and Clarke 1987:164-206). On the one hand, waterlogged wood is very heavy due to the weight of the contained water. On the other hand, the wood is very soft and fragile due to the chemical and biological degradation processes that it experienced (Grattan 1987:55-67). The main challenge in the conservation of waterlogged wood, is to dry the wood (i.e., extracting the water within the wood) in such a way that subsequent collapse and shrinkage of the wood structure can be minimized or avoided. An approach to address this challenge is based on the idea of impregnating the wood with a consolidant, which would confer mechanical strength to the wood while the water is being removed (Grattan and Clarke 1987:164-206). Different consolidants have been tested for this purpose, but probably the most accepted material is a water-soluble synthetic wax: Polyethylene Glycol (PEG).

An example of the challenges that conservation of waterlogged wood represents is the Swedish Royal Warship *Vasa*. The flagship of the seventeenth-century Swedish fleet sank on August 10, 1628, in Stockholm harbor during its maiden trip (Franzén 1961:10; F. Hocker 2006:53). The shipwreck was relocated in 1956, revealing that the majority of the ship was in a good state of preservation (Franzén, 1961:13-14; Cederlund and F. Hocker 2006:172-179). From the 1950s to the 1980s, the *Vasa* and all its

contents were raised from the seabed (Cederlund 2006) and conserved with PEG (Barkman 1965; 1967; 1975; 1976; Håfors 2001). After its conservation was concluded, the *Vasa*'s hull and hundreds of wooden objects from the circa 25,000 artifacts of the *Vasa*'s collection started to develop acidic salt outbreaks (T. Sandström et al. 2001:56; M. Sandström et al. 2001, 2002a, 2000b; E. Hocker 2006:19). The origin of these outbreaks was an unforeseen reaction from sulfur, from the waters of Stockholm harbor, and iron compounds diffused in the wood (M. Sandström et al. 2001; 2002a; 2002b; 2003). Researchers estimate that up to 2,000 kg of sulfuric acid has already been formed inside the hull (M. Sandström et al. 2001:68; M. Sandström et al. 2003:41, Almkvist et al. 2004:203).

Since the discovery of the outbreaks, suitable re-conservation methods for the hundreds of affected wooden artifacts have been under study. Recently, researchers found a way to successfully extract the iron compounds from wooden samples from the *Vasa* collection. By removing the iron compounds from the wood, the sulfuric reactions are prevented. The method uses a chelating agent, EDTA, to effectively remove iron compounds from wood (M. Sandström et al. 2003:50-55; Almkvist et al. 2004). However, long-term stability of the results and harmlessness of the treatment are under evaluation (E. Hocker 2006:19). Once a solution will be applied to the endangered wooden artifacts, the next step for the *Vasa* collection should be the selection of a re-conservation method for them. To achieve this goal, the *Vasa* Museum research program is examining different conservation methods on *Vasa* wood.

In the 1990s, researchers at Texas A&M University (TAMU) started to develop a series of procedures involving alkoxysilanes for the conservation of archaeological waterlogged materials ((1998) US Pat 5, 789.087; (2000) US Pat 6, 020, 027; (2002) US Pat 6, 432, 553; (2004) US-Pat 6, 835, 411; (2005) US Pat 6, 881, 435; Smith 2003). One study derived of this initial research proposed the use of alkoxysilanes for re-treating artifacts previously conserved by impregnation with PEG (Smith 1998, 2003:30-59). The study, presented in this thesis, applies, continues, and expands upon previous studies with alkoxysilanes by researches from TAMU.

In 2007, the author contacted the *Vasa* Museum to explore the feasibility of re-treating artifacts previously conserved by PEG impregnation with alkoxysilanes. The study tried to evaluate pros and cons of re-conserving artifacts with this type of silanes. After developing a research design in conjunction with the *Vasa*'s conservation unit, a series of experiments were conducted focusing on small, organic, waterlogged wood samples from the *Vasa* Museum Collection, to test three different re-conservation methods. The experiments were carried out at the Conservation Research Laboratory (CRL) and the Archaeological Preservation Research Laboratory (APRL) at TAMU during 2007 and 2008. The research constituted the core of the present MA Thesis at TAMU and, hence, falls outside the main research project initiated by the *Vasa* Museum.

### **Brief History of the *Vasa***

The history and events associated with the seventeenth-century royal warship the *Vasa* (Figure 1) are not only some of the most fascinating episodes of Swedish history, but are also some of the most remarkable events to have occurred in maritime history during modern times.



Figure 1. The *Vasa* at the hall of its Museum in Stockholm, Sweden (Courtesy Archives, the Swedish National Maritime Museums. Photographer, Anneli Karlsson).

The historical events related to the sinking of the *Vasa* have been debated by historians for more than four centuries (Cederlund 2006:109-114). More recently, in the second half of the twentieth century, the relocation of the ship, its recovery from the

seabed, excavation, study, and pioneering process of conservation have noticeably improved the knowledge about the maritime history of the seventeenth century, the *Vasa* itself and the cause of its sinking. All these new technological accomplishments and the subsequent academic studies have dramatically increased the number of books and scientific articles directly devoted to the *Vasa*.

Consequently, to summarize the history of the *Vasa*, its sinking, and recovery would not only be quite an extensive enterprise in general, but also an unsuitable purpose for this MA thesis. The *Vasa* Museum in Stockholm is publishing a series of detailed scientific books that will undertake the ambitious assignment of summarizing the numerous events that define the history of the *Vasa*. This projected scientific summary has started to be published, and the first volume, authored by Carl Olof Cederlund and edited by Fred Hocker, is published elsewhere (Cederlund 2006).

Nevertheless, for a better understanding of the overall context in which this MA thesis falls, a brief history of the ship and its sinking will be presented. In addition, a more detailed history of the process of conservation that the *Vasa* and its collection has undergone will also be presented.

Throughout this chapter, there are some instances in which *Wasa* is used instead of *Vasa*. From the beginning of the *Vasa* Project there has been a debate about what the proper spelling of the ship's name should be, *Wasa* or *Vasa*. In the late 1980s, based on linguistic grounds and because it was thought to facilitate communication, it was decided to spell the ship's name in its modern spelling, *Vasa*. However, names of organizations that were created before the convention was adopted, and therefore used the old spelling

(i.e., *Wasa*), have not been modernized as those were their legal names (Cederlund 2006:15-16).

The period from the reign of Gustav II Adolf (1611-1632) through the wars of Carl XII (1697-1718) is known in the history of Sweden as the Age of Greatness or the Great Power Period. In slightly over one hundred years, Sweden transformed itself from a small, under-developed kingdom on the outer reaches of Europe to one of the central players in continental politics. King Gustav II Adolf is a central figure in this period and in the history of the *Vasa*, not only because he ordered the ship, but also because he was an active participant in the planning of the ship's armament (F. Hocker 2006:36).

During the 1620s, Sweden, as a belligerent nation involved in the group of related conflicts now known as the Thirty Years War, was defending and trying to expand its territory south of the Baltic Sea. In the tactics of the time, the naval fleet was of the utmost importance for convoy troops and to blockade enemy troops (F. Hocker 2006:38-39).

In the decades before the 1620s, the Swedish naval fleet was primarily composed of small-ships from which its main combatant vessels had a single deck of 12-pounder cannons. The King of Sweden, Gustav II Adolf, planned to change this policy and decided to enlarge his fleet. He contracted with the state shipyards for the construction of five large, two-decked ships armed with heavier guns to become the backbone of the Swedish fleet: *Vasa*, *Äpplet*, *Scepter*, *Kronan*, and *Göta Ark* (F. Hocker 2006:39).

In January 1625, a contract for the operation of the Stockholm Naval Shipyard was signed with two Dutch brothers, Henrik Hybertson and Arendt Hybertson de Groot.

The former was a naval architect and former shipbuilder at the Stockholm Naval Shipyard; the latter was a businessman with good contacts with suppliers both in Sweden and in Holland. The contract included the construction of four new ships, two larger and two smaller ones (F. Hocker 2006:41-42).

Originally, the length of the keel of the larger vessels was ordered by the King to be 136 feet (40.4 m). Yet in the final version of the contract signed by the King, the length of the keel of the larger vessels was reduced to 128 feet (38.0 m). The two smaller ones were to be built to the same size of an existing ship, the *Gustavus*, which had a keel length of 108 feet (32.1 m) (F. Hocker 2006:42-43).

The Hybertsons spent the rest of 1625 purchasing timber, and by the end of the year they had adequate wood to begin constructing either a large or a small ship. Preparations were made to begin constructing one of the smaller ships. In the fall of 1625, however, the Swedish naval fleet lost ten ships in a storm on their voyage home from battles in the south Baltic. Among them were several large ships, and the King decided to make up for the loss as soon as possible. Consequently, he wrote Admiral Fleming telling him to inform Hybertson that two medium-sized ships must be constructed, and they should have a keel length of 120 feet (35.6 m) (F. Hocker 2006:43).

The new request with new specifications from the King caused a great deal of trouble for Hybertson, who had collected timber for either a large or a small ship and, furthermore, had already laid the keel for one of the smaller ships. After disagreeing with the King's wishes and his new specifications, Hybertson managed to get his way

due to the King's immediate need for a vessel. Finally, Hybertson notified the King that he would start to build one of the larger originally commissioned vessels, yet the ship would be slightly smaller than the specification (F. Hocker 2006:43).

This comment from Hybertson has been the origin of a widely accepted hypothesis that maintains that the keel of the *Vasa* was lengthened from the 108 feet of the smaller commissioned ship to the King's new specifications of 120 feet. It was believed that as a result of this, and other changes requested by the King, the ship's construction was flawed, and that was one of the reasons why the ship sank (Borgenstam and Sandström 1984; Landström 1980:44-49). However, this widely accepted hypothesis has been recently dismissed (F. Hocker 2006:44). According with the archaeological remains of the ship, it has been shown that the *Vasa* was actually built following the original specifications of the contract but was a little shorter, just as Hybertson reported. The keel of the *Vasa* is constructed from four pieces joined together. Its length is closer to 130.5 feet long, hence a little shorter than the original specification of 136 feet (F. Hocker 2006:44-46).

The keel of the *Vasa* was laid late in the year 1625, and it was probably launched in the summer of 1626, which means a very short building period for the hull. Besides the nautical construction, the ship had another function to serve. Its name, *Vasa*, was the name of the ruling house, and the King wanted the vessel to serve as propaganda, presenting him as one of the great princes of Europe. For this purpose, an elaborate program of sculptural decoration, brightly painted and shaded in polychrome style, was carved with over 700 different elements (Scoop 1986; F. Hocker 2006:46-47).



In 1625 the King ordered the casting of 72 new, standardized 24-pounder bronze guns for the new ship. The standardization of the size of the cannons that the ship would carry was a major warfare innovation at the time (F. Hocker 2006:47-52). Hence, when the *Vasa* sailed in 1628, and despite the fact that the vessel was short eight of the guns that it was supposed to be armed with (i.e., it was carrying 64 guns), it was the most powerful warship in northern Europe in terms of firepower (F. Hocker 2006:44-49).

Once the construction of the ship was completed, the vessel was armed and equipped; the *Vasa* was ready to sail for its first time. Its maiden trip was scheduled on August 10, 1628. According to sources, the day was a summer Sunday with clear skies and a gentle southerly breeze (Franzén 1961:10; F. Hocker 2006:53). Due to the planned short length of the maiden trip, some relatives of the sailors had boarded to accompany the ship on its first trip through the Stockholm archipelago (F. Hocker 2006:53).

About three or four in the afternoon, the captain of the vessel, Hansson Söfring, ordered to cast off and set the sails of the new warship of King Gustav II Adolf of Sweden (Franzén 1961:10). After the initial maneuvers, and in accordance with naval traditions, the cannons were run out in order to perform a salute by shooting the ship's guns as the ship left the town (F. Hocker 2006:53). The roar of the guns echoed in the ears of the numerous people who had gone to wave farewell to the ship. The King was not present, but among the public were dignitaries and foreign diplomats interested in the new warship of King Gustav II Adolf of Sweden (F. Hocker 2006:36).

Unexpectedly, the maiden voyage of the *Vasa* would not go beyond 1500 meters (F. Hocker 2006:36). A gust of wind heeled the ship, the water started coming through

the gunports of the lower gun deck, and the ship sank in the cold waters of the harbor of Stockholm (Franzén 1961:10; F. Hocker 2006:53).

The historical accounts revealed that about 150 people were on board, from which it is estimated that probably 30 but perhaps up to 50 died, including women and children (F. Hocker 2006:55).

The unexpected sinking of the *Vasa* was a national catastrophe. The reaction from the authorities was swift, and the sinking of the *Vasa* was followed by an investigation. Even though the inquest reached some conclusions about the reasons for the sinking, a specific cause was not found, and no one in particular was to blame, to be punished or convicted (Franzén 1961:10-11; Cederlund 2006:55-58).

Salvage attempts to recover the ship immediately followed the sinking. The English engineer Ian Bulmer led several attempts to recover the ship (Franzén 1961:12; F. Hocker 2006:55, Hafström and F. Hocker 2006:69-71). After the sinking, it was realized that the main mast protruded at an angle, and Bulmer managed to straighten the hull (Franzén 1961:12; F. Hocker, 2006:55). However, efforts to reposition and re-float the vessel were unsuccessful, and their only achievement was to push the ship farther down into the bottom clay of the bay (Franzén 1961:12; Hafström and F. Hocker 2006:69).

In 1663, the Swede Hans Albrekt von Treileben proposed to rescue the 24-pound bronze cannons by using a diving bell. After received permission from the authorities, he partnered with the German Andreas Peckell (Hafström and F. Hocker 2006:79-98). They managed to rescue 53 of the *Vasa*'s guns (Hafström and F. Hocker 2006:92).

During the 1680s, one last salvage operation to rescue the ship was conducted in which at least one more gun was recovered (Hafström and F. Hocker 2006:95-98). After all these salvage operations conducted during the seventeenth century, and due to the methods used to attempt to recover the ship and its cannons, the majority of the rigging elements and some parts of the main deck were destroyed (Hafström and F. Hocker 2006:106).

During the nineteenth century, the development of the heavy diving dress and other diving apparatus, followed by their introduction to Sweden, allowed these pioneer hard-hat divers to visit the shipwreck on at least three occasions (Cederlund 2006:113-122). Later, in the 1920s, following the recent discovery and salvage of the wreck *Riksnyscheln*, there was a proposal by a diving company to salvage the *Vasa* (Cederlund 2006:126-130).

Despite the interest surrounding the *Vasa* in the three centuries immediately following its sinking, the precise location of the wreck was unknown in the mid-twentieth century. Finally, in the 1950s Anders Franzén, an engineer and lover of naval history, was able to relocate the shipwreck through his passion and research. More important, his determination, personality, and marketing skills were essential to revive the interest in the lost ship. Franzén created the right conditions, and organized and planned a project that ultimately would raise the ship and its contents in their entirety for preservation and exhibition (Cederlund 2006:140-142).

Franzén began the arduous task of searching files and prospecting in the bay that took three years to bear fruit (Franzén, 1961:13; Cederlund and F. Hocker 2006:172-

178). With a gravity-powered coring device of Franzén's own design, he started to prospect a predetermined area of the Stockholm harbor (Cederlund and F. Hocker 2006:175-179). In August 1956, Franzén, working with salvage diver Per Edvin Fåltning and the Swedish navy, picked up pieces of black oak that gave them an indication that they had relocated the *Vasa* (Franzén 1961:13; Cederlund and F. Hocker 2006:178).

Franzén persuaded the Swedish navy to let its divers investigate the shipwreck further (Franzén 1961:13-14; Cederlund and F. Hocker 2006:179-185; Cederlund 2006:185-216). During these first dives on the shipwreck, the excellent preservation of the ship was discovered. This optimal preservation status was the result of several factors: no attack of so called "shipworms" had occurred due to the lack of marine wood-boring mollusks (i.e., *Teredo sp.*) in the Baltic; the lack of oxygen and the low temperature of the cold waters of the Stockholm archipelago; and finally the fact that when the *Vasa* sank it was a brand new ship (Barkman 1965:4; E. Hocker 2006:16). Probably it was then when Franzén started to envision the possibilities, realizing and organizing a project with the ultimate goal of raising the ship and its contents (Cederlund 2006:140-142).

In 1957, the *Vasa* Committee was created providing the institutional framework in which the *Vasa* project could be carried out (Cederlund 2006:185-216). The *Vasa* Committee decided that the excellent preservation of the ship justified its lifting and preservation. Therefore, six tunnels under the hull were to be made in order to pass through cables, which would lift the ship using two large pontoons (Franzén 1961:14-18; Cederlund 2006:217-290). The idea was to lift the ship sufficiently to allow divers,

working under water, to prepare the ship, tightening the structure and making it watertight for the final lifting (Cederlund 2006:285-290).

The *Vasa*, after being prepared for the final lift, could go into dry dock without the aid of the salvage fleet, which could not tow the ship to the interior of the dock (Cederlund 2006:290). It was decided to place the ship on a floating pontoon which was custom-built for the project. In this floating pontoon, on which the *Vasa* still stands, the ship was eventually conserved and displayed (Håfors 2001:19-21; Cederlund 2006:275).

Despite the technological challenge and extreme difficulty of the diving and engineering operations conducted to recover the ship, the effort was rewarded. On April 24, 1961, at 9:03 am the timbers of the *Vasa* saw the sunlight again (Figure 2) after 333 years in darkness at the bottom of the harbor of Stockholm (Cederlund 2006:290).

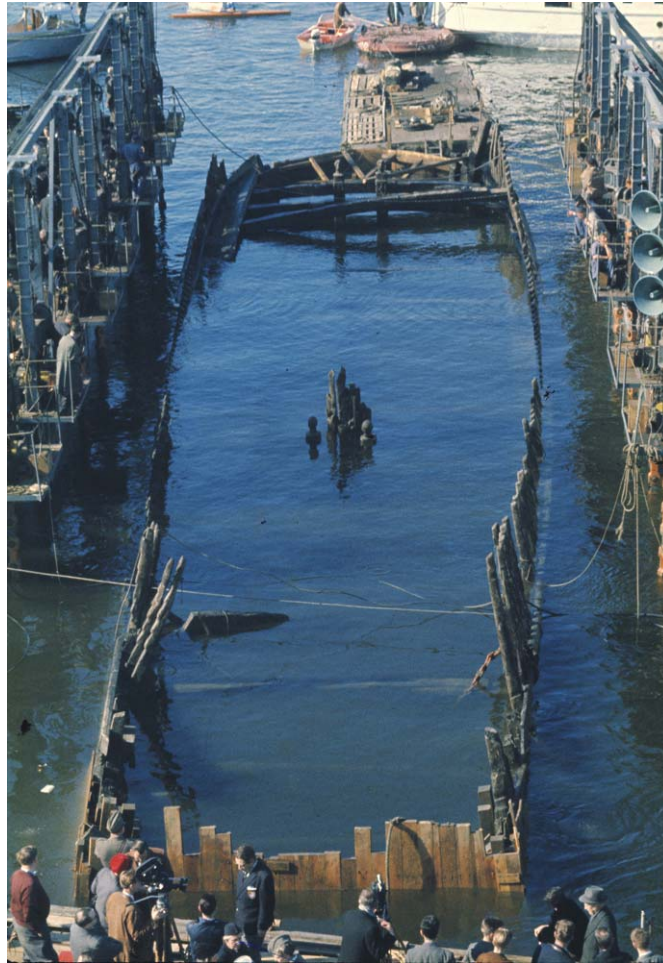


Figure 2. The *Vasa* being lifted to the surface on April 24, 1961 (Courtesy Archives, the Swedish National Maritime Museums).

After the lifting of the ship, diving operations continued on the *Vasa* wreck underwater site from 1964 to 1967 in which almost 2,000 new finds were recovered (Håfors 2001:5; Cederlund 2006:457-472).

After the final lifting, the *Vasa* hull was reinforced on the floating pontoon in the dry dock (Figure 3). The ca 5,500 iron bolts originally holding the structure together totally rusted away underwater and, therefore, had to be replaced (Roth and Malmberg 2004:174; Hocker et al. 2007:470). The Conservation Council recommended using

stainless steel, but this recommendation was not adopted because of the high cost. Thus, the original corroded, iron bolts were replaced with new epoxy-coated galvanized mild steel bolts (Håfors 2001:30-31; M. Sandström et al. 2001:69, 88; Cederlund 2006:429).



Figure 3. The *Vasa* hull reinforced on the floating pontoon in the dry dock (Courtesy Archives, the Swedish National Maritime Museums).

During the summer of 1961, the whole interior of the ship was completely and systematically excavated following archeological standards (Figure 4) (Cederlund 2006:292-400). The archaeological excavation, led by Senior Archaeologist Per Lundström, recovered 16,000 registered finds (Håfors 2001:4). Due to a curatorial decision made in the 1990s, the groups of objects originally cataloged as a single number have been renumbered as individual items; the total number of finds within the ship has thus risen to more than 19,000 as of October 2005 (Cederlund:304).



Figure 4. Carl Olof Cederlund during the excavation of the *Vasa* (Courtesy Archives, the Swedish National Maritime Museums).

In 1961 after the archaeological excavation was completed, a superstructure was built on the floating pontoon (Figure 5). At the end of the year, the pontoon superstructure was closed with walls and a roof of aluminum sheets. The enclosed superstructure was then moved to where the temporary *Vasa* museum was under construction (Figure 6). The temporary museum called *Wasavarvet* (i.e. *Wasa* Shipyard) was open to the public from 1962 to 1988. *Wasavarvet* was responsible for the processing of the finds, the conservation of the ship's hull and its collection, and the assembly and restoration of the vessel (Håfors 2001:22-41; Cederlund 2006:422-456).





Figure 5. Superstructure built over the *Vasa* on the floating pontoon. Left, superstructure of concrete beams; Right, final enclosed superstructure (Courtesy Archives, the Swedish National Maritime Museums).



Figure 6. *Wasavarvet*, *Vasa*'s temporary museum (1962-1988). *Vasa* and its collection of artifacts were conserved at the *Wasavarvet*. Note the final enclosed superstructure in the back of the image (Courtesy Archives, the Swedish National Maritime Museums).

Several academic studies have been devoted to explaining the reasons why the *Vasa* sank. In overall terms, the ship sank due to the succession of several different factors that led to the catastrophe. Among the most crucial errors the following stand out: the design was flawed; the construction process was not properly managed; a failed stability test was ignored by the captain and the navy; the ship was put to sea in a dangerous state (lacking ballast and being unstable); and, finally, the ship sailed with the gunports open. The compilation of these errors contributed to and led to the unpredicted outcome of the *Vasa's* maiden trip (F. Hocker 2006:58-60).

### **The Conservation of the *Vasa***

The conservation and restoration of the *Vasa* is, without doubt, one of the largest projects of conservation and restoration ever undertaken by man (Barkman 1965:7; 1975:82; 1976:52). Not only did it accomplish, for the first time in history, the conservation of the complete hull of a ship of the dimensions of the *Vasa* (Barkman 1975:82; 1976:52; Håfors 1990:195-216; 2001:63; M. Sandström et al. 2001:69; E. Hocker et al. 2007:477), but more than 24,000 objects were also preserved (Barkman 1965:11). The scope and complexity of the conservation of the *Vasa* has produced numerous scientific articles, academic theses, and dissertations, and a few books. A detailed summary of the conservation of the *Vasa* can be found elsewhere (Håfors 2001). Nevertheless, a brief summary of the conservation of the *Vasa's* hull and its collection will be presented here for a better understanding of the overall context of this MA thesis.

The *Wasa* Board was created to succeed the *Wasa* Committee in 1959. The Board took over all responsibility for the *Vasa* project including its preservation (Håfors 2001:7; Cederlund 2006:185). Due to the number and diversity of objects retrieved, and also due to the complexity of its preservation, in 1961 the *Wasa* Board created a board of scientific and engineering specialists that was called the Conservation Council of the Board of the *Vasa*. In 1964 when responsibility for the *Vasa* was transferred to the Swedish National Maritime Museum, the Conservation Council of the Board of the *Vasa* ceased to exist. However, soon after a new Conservation Council for the Conservation of the *Vasa* was created (Håfors 2001:8-11).

The principal challenge of the conservation process was all the wooden elements from the hull of the *Vasa* and the thousands of loose objects. As explained in more detail later, waterlogged wood keeps its shape because its cellular structure is filled with water. If water evaporates, the wood structure begins to shrink and crack. Finally, the timbers collapse within days of being in contact with the atmosphere (Grattan 1987:55-67). Therefore, the *Vasa* had to be preserved with a method that allowed the extraction of water, avoiding the collapse of the wood.

In 1961, Lars Barkman, a chemical engineer, was employed as the full-time conservation manager and head of the conservation department. He held the post of the head of the conservation department until 1978 when Birgitta Håfors, the research and analytical chemist of the project, succeeded him (Håfors 2001:11).

Extensive research work was conducted in order to withstand the challenges derived from conserving a ship of ca. 1200 tons, 69 m (226 ft) in length, 11.7 m (38 ft)

in beam, plus the more than 24,000 artifacts as of 1964 (Barkman 1965; 1967; 1975; 1976).

The method selected to preserve the wood was to stabilize it with polyethylene glycol (PEG), a synthetic wax that can be mixed with water. PEG is manufactured in different molecular weights, and has the ability to penetrate into the wood and replace the water in it, drying gradually and avoiding collapse. Although the technique was known, it had never been attempted to conserve such a large volume of waterlogged wood (Barkman 1975:65; Håfors 1990:195-216; 2001:63; M. Sandström et al. 2001:69; Hocker et al. 2007:477).

The unprecedented undertaking entailed the preservation of a volume of 707,921 m<sup>3</sup> (25,000 cubic feet) of waterlogged wood, with a total surface area of 13,935 m<sup>2</sup> (150,000 square feet), and in which a total 580 tons of water had to be extracted from the entire hull (Barkman 1975:65; 1976:53).

After the preliminary research, the more than 24,000 objects were prepared to be conserved with impregnation with PEG. In the case of the objects, the successful impregnation was achieved by immersing them in a heated solution of PEG. The first treatment tried was a bath containing 30% of PEG 4000 which was heated to 25 °C; after immersing the object the temperature was progressively increased until 90 °C was reached; at the same time the concentration of PEG 4000 gradually increased to 100%. It was found that this treatment could obstruct the cells, thus preventing further penetration of the PEG, which could lead to wood collapse. The second approach was to start the bath with a concentration of 5% or less PEG 4000 at an even temperature of 60° C and

progressively increase the PEG 4000 concentration to 100%. It was also found that PEG 1500 achieved better penetration than PEG 4000. The vast majority of the wooden finds from the *Vasa* were treated following this heated PEG impregnation method in twenty-one batches from 1962 to 1978 (Håfors 1993:52). To avoid undesired biological growth during treatment, a mixture of boric acid and borax was mixed into the PEG solution, as explained later in more detail (Barkman 1965:8-13; 1975:71-82; 1976:50-53).

The described PEG impregnation treatment produced poor results on highly degraded and fragile wood objects. Therefore, these objects were stored in freshwater tanks until a suitable conservation treatment was devised. These finds were conserved during the 1970s by pre-treatment with a solution of 5% to 10% PEG 400 and followed by freeze-drying (Barkman et al. 1976:17-26; Hocker et al. 2007:478).

As previously mentioned, the main challenge of the conservation process was the hull of the *Vasa*. The method selected to extract the water from the hull was spraying the wood with PEG. Because spray treatment with PEG on a large scale had never been performed before, it was decided to carry out a large-scale test before the treatment of the *Vasa* was started. Timbers from other contemporary wrecks from just outside the Stockholm harbor were salvaged by the Swedish navy in order to build four test panels of 1.5 by 1.5 meters. PEG 4000 was tested by itself on one panel and in combination with PEG 1500 on the other two panels, keeping the fourth panel as a control reference. The conclusions of the test panels were that the diffusion of the PEG was very slow and had to be promoted by maintaining high water content in the wood by maintaining a high

relative humidity in the surrounding air during the diffusion period (Barkman 1975:82-94; Håfors 2001:51-54).

It was decided that the hull would be sprayed daily with a solution of PEG. During the period in which the hull was in the open air, it was sprayed with sea water in order to avoid uncontrolled drying. As a consequence, green algae appeared on the outside surfaces. Therefore, an aqueous solution of sodium pentachlorophenate (NaPCP) was chosen to address the surface growths. Thus, in addition to the daily spray of PEG solutions, from April 1962 until the end of 1963, one round per month of NaPCP solution was sprayed onto the hull (Håfors 2001:55-56).

It was suggested that in addition to the commercial fungicides, the *Vasa* conservation laboratory should have composed a formula on its own based on borates. Thus, after conducting an experiment with different mixtures, a mixture of seven parts of boric acid and three parts of borax was chosen as a fungicide treatment for the conservation of the *Vasa*. Beginning in July 1962, the preservation solution was put into use with a composition of 15% PEG 4000 and 6% boric acid – a borax mixture in the proportions 7:3 for the exterior surfaces of the *Vasa* hull. However, to achieve a sufficient penetration into the interior of the hull, a similar preservation solution was applied with the distinction that it was prepared with PEG 1500 instead of PEG 4000 (Barkman 1967:8-11; Håfors 2001:55-58; E. Hocker 2006:17).

The spraying of the solution of PEG 4000 was carried out by hand by two teams and took five hours to complete one round of the treatment; these treatments were conducted from April 1962 to March 1965 when an automatic spraying system was

installed. In total, the hand-spraying operations had consumed 130 tons of PEG and 50 tons of borate formula (Håfors 2001:58).

In 1964, it was suggested that PEG 1500 could be more suitable than PEG 4000 for the spray treatment. Therefore, it was decided that from 1965 the hull of the *Vasa* was automatically sprayed (Figure 7) several times a day with a solution of PEG 1500 and water (Håfors 1998:89; 2001:63; T. Sandström et al. 2001:57). The number of spraying rounds decreased progressively within time from 32 rounds per 24-hour period in 1965 to one round per 24-hour period in 1979 (Håfors 2001:63-64).



Figure 7. The *Vasa* being conserved through the automatic spraying system (Courtesy Archives, the Swedish National Maritime Museums).

In 1971 it was decided that PEG 600, due to its greater dimension-stabilizing effect, should be used instead of PEG 1500. Thus, from March 1971 to January 1979, PEG 600 progressively replaced PEG 1500 in the preservation solution (Håfors 2001:64-65; E. Hocker 2006:17).

It was decided that the preservation solution should start with a low PEG concentration and end with a rather high one. A PEG concentration of 10% was chosen for the start of the preservation process and 45% as an end concentration. The main principle when deciding to increase the PEG concentration was that equilibrium had been established between the PEG concentration in the solution and the PEG concentration in the wood. The PEG content of the wood was determined by analyzing several core samples throughout the process. The equilibrium of the PEG concentration ultimately determined the length of the treatment (Håfors 2001:65).

In August 1974, due partly to economic reasons, a suggestion was made at the Conservation Council meeting to establish the point in time when the spray treatment was to be finished. At that moment, the equilibrium between the 35% PEG in the solution and PEG in the wood had not yet been established. To find a quicker way to reach the end-point of the conservation treatment, it was suggested that the PEG concentration should be raised to 50%. Soon after, in the next meeting of the Conservation Council, Barkman reported that the concentration had been raised to 43%, and in his opinion it was not advisable to raise the concentration further. The PEG concentration was kept at about 45% during the remaining four years and four months of spraying with the automatic system (Håfors 2001:67-68).



In November 1974, it was suggested that the treatment should be finished when the desired PEG-ratio had been reached in the wood. The Conservation Council suggested that it should be safe to end the spray treatment. As a consequence, a trial stoppage did start in January 1975. Barkman, at this time, had expressed apprehension that the drying of the timbers might be going too fast. Twelve inspections were performed in 1975 to decide if the spray treatment should be restarted. From these inspections, three different plans for ending the spray treatment of the *Vasa* hull were presented and discussed in February 1976. The first scheme was proposed by Barkman, who suggested raising the number of spray rounds per day and continuing the spray treatment for a period not longer than eight years (i.e. 1984). The second proposal was to continue spraying at the same pace until the end of 1976 and then continue at a lower pace until the end of 1977. The third proposal was to lower the pace immediately and stop the spray treatment at the end of 1976. The Conservation Council recommended following the second proposal, and soon after it was confirmed by the museum (Håfors 2001:68-69).

As Barkman did not agree that this would be the most suitable way of treating the *Vasa* hull, he appealed to the Swedish government to annul the decision that had been made by the museum, and suggested adopting the plan that he had recommended for the treatment of the *Vasa* hull (Barkman 1976:53). The Swedish government request two expert opinions from two independent sources: the National Museum of Denmark and the Swedish Institute of Wood Research. Both independent reports, and a third one by a conservators' organization, concluded that the spray should be continued. Despite the

reports received, on September 1977 the government drew the conclusion that there was no reason to invalidate the decision made by the museum of continuing spraying until the end of 1977. Under the circumstances, Barkman felt that he no longer could take responsibility for the conservation management and, therefore, resigned his position in October 1978 (Håfors 2001:69-70).

After Barkman's resignation, the data for PEG and water contents were examined, and inspections and measurements indicated a rather stable situation of the hull. However, it had been noted that the moisture ratio values were higher by 13% in the inner planking than in the outer planking. Håfors, who had replaced Barkman as head of the conservation department, agreed about accelerating drying of the hull's interior by improving ventilation yet recommended the spraying be continued (Håfors 2001:70-71). In December 1978, the Conservation Council recommended that the spraying with PEG 600 should be stopped for a supervision period of three months. The museum ordered to stop the automatic spray system on January 22, 1979 (Håfors 2001:75-76). During the automatic spraying of the *Vasa* hull, from 1965 to 1979, 240 tons of PEG and nearly 15 tons of borates were consumed by the system (Håfors 2001:71-73). During the complete spraying of the hull, from 1962 to 1979, the spray treatment for the *Vasa* hull consumed a total of 370 tons of PEG and nearly 65 tons of borates.

From 1979 to 1989, when the ship was moved to the permanent *Vasa* Museum, the treated wood was progressively allowed to dry by controlled air drying (Håfors 1984; 2001:85-107). In those years, the upper structure of the ship was reconstructed and the

sculptures reattached to their original position. A final surface treatment was applied on all the surfaces of the wood. A solution of 45% PEG 4000 was sprayed several times to create a thick layer that would protect the wood during the transportation to the museum. After the ship was moved its permanent museum (Figure 8), and after the ship was cleaned from construction dust, the PEG 4000 from the surfaces of the hull was melted with hot air blowers in order to get it closer to the original texture of the wood (Håfors 2001:76-83). After the final surface treatments, the conservation of the *Vasa* was considered to be concluded. Yet maintenance cleanings of the ship's surfaces were scheduled and periodically performed after the museum was officially opened in 1990 (Håfors 2001:83).

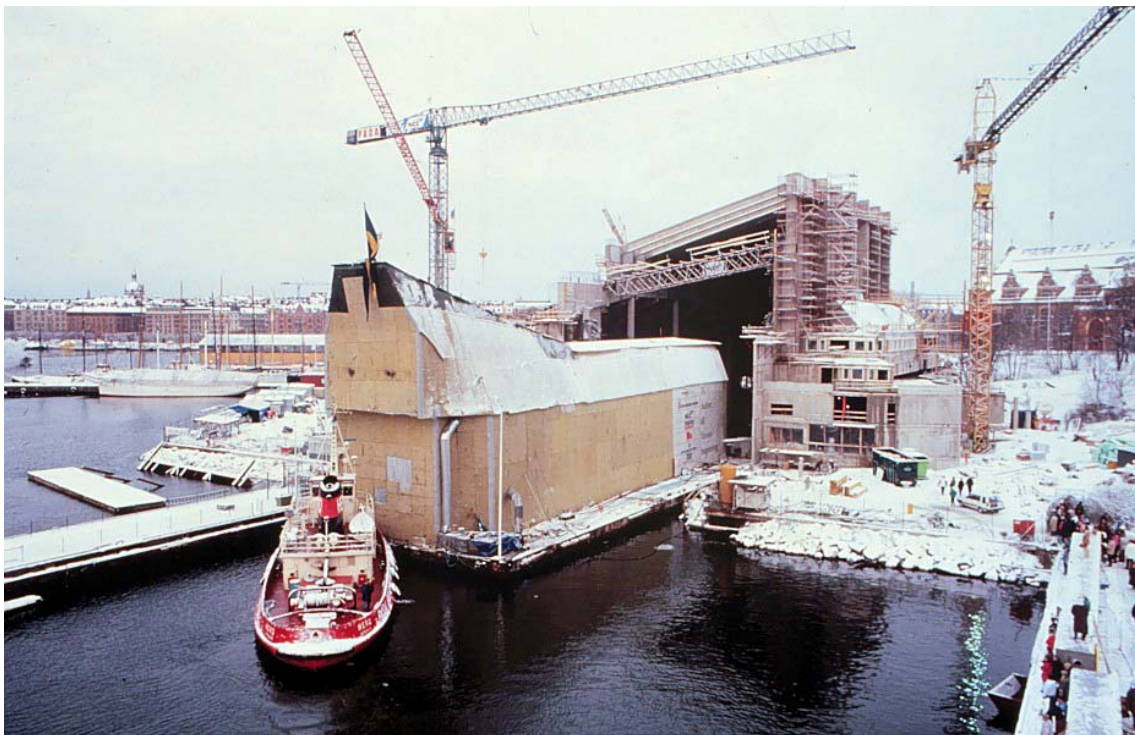


Figure 8. The ship being transported to the permanent *Vasa* Museum (Courtesy Archives, the Swedish National Maritime Museums).

Unexpectedly, the conservation of the *Vasa* did not end in 1990. In the summer of 2000, it was discovered that some areas of wood in the hull and some wooden artifacts, were starting to ooze white and yellow acidic salt precipitations (T. Sandström et al. 2001:56; M. Sandström et al. 2001, 2002a, 2000b; Roth. and Malmberg 2004:171; Fors 2005:23; Hocker et al. 2007:469). These precipitations or outbreaks (Figure 9) were detected in the early 1990s by an observant conservation technician, but it was not until the wet summer of 2000 that the problem was found to be widespread. During the summer of 2000 a record number of visitors to the museum caused the relative humidity within the ship's hall and stores to exceed levels of 65% (E. Hocker 2006:17; Hocker et al. 2007:469).



Figure 9. Acidic salt precipitations (Courtesy Archives, the Swedish National Maritime Museums. Photographer, Emma Hocker).

The affected areas by the precipitations were often softer than surrounding wood, and showed pH levels of less than three and sometimes as low as one. Core samples to be analyzed were taken from various places around the ship. The analyses revealed the deposits to be sulfur salts: yellow natrojarosite, bluish-white melanterite, ordinary white gypsum, and elemental sulfur (M. Sandström et al. 2001, 2002a, 2002b; 2003; Fors 2005; E. Hocker 2006: 17-18; Hocker et al. 2007:469).

Sulfur had penetrated into the wood during the 333 years that the ship remained at the bottom of Stockholm harbor that was polluted by sulphate-rich natural sewage (M. Sandström et al. 2001:69; T. Sandström et al. 2001:58; M. Sandström et al. 2003:35:69 Roth and Malmberg 2004:172; Almkvist 2004:203; Fors 2005:16-23; Hocker et al. 2007:470).

The sulfur deposits had reacted with the atmospheric oxygen, producing sulfuric acid. This chemical reaction normally occurs at a slow pace, but in the case of the *Vasa*, iron compounds from the oxidation of the more than 5,500 original bolts the hull originally had, plus the humid environment in the summer of 2000, catalyzed (i.e., accelerated) the reaction (M. Sandström et al. 2001:69, 88; T. Sandström et al. 2001:58; M. Sandström et al. 2003:38-39; Almkvist 2004:203; Roth and Malmberg 2004:174; Hocker et al. 2007:470). These sulfur reactions have been described thoroughly elsewhere (M. Sandström et al. 2001; 2002a; 2002b; 2003).

In 2003, it was estimated that two tons of sulfuric acid had formed in the hull of the *Vasa* (M. Sandström et al. 2001:68; M. Sandström et al. 2003:41, Almkvist et al. 2004:203). This corrosive acid put the preservation of the *Vasa* in serious jeopardy (M.

Sandström et al. 2001:68; Hocker et al. 2007:470). As a consequence, an international research project, *Preserve the Vasa Project* (2003-2006), was launched to study the problem and try to find solutions. Experts from around the world developed several research programs to identify, analyze, and address the problem (Roth and Malmberg 2004; E. Hocker 2006:18; Hocker et al. 2007:470).

Early on, it was realized that the problem was very complex, but the conclusion was drawn that there were two factors of the problem from which preliminary remedies could be achieved. The first factor was the necessity of immediately neutralizing the sulfuric acid present in the wood (T. Sandström et al. 2001:65). Therefore, it was necessary and urgent to increase the pH in the acidified wood/wood surfaces (M. Sandström et al. 2001:68). The second factor that influenced the outbreaks of 2000 was the high levels of relative humidity reached. Therefore, it was suggested that a more stringent control of the climate and more moderate temperature level was of prime concern. Thus, the relative humidity of the museum was lowered substantially (M. Sandström et al. 2001:68).

In order to mitigate the threat of the sulfuric acid in the outbreaks on the *Vasa's* hull, alkaline solutions were applied from 2001 to 2005 to neutralize the acid by increasing the pH levels (M. Sandström et al. 2002b:84, 86; M. Sandström et al. 2003:47; E. Hocker 2006:18-19; Hocker et al. 2007:478).

More complex and ambitious neutralization treatments for the acidic outbreaks have been proposed, such as the use of nanoparticles of calcium hydroxide (Giorgi et al. 2005, 2007) and the use of ammonia vapour (Fors et al. 2007).

Furthermore, in 2004, to control the relative humidity of the museum, a new climate system was installed in the ship hall, stabilizing the climate. Since the installation of the new climate system, the hall of the museum has been maintained at 55% RH (+/- 4%) and 18-20 °C (+/- 2 °C) (E. Hocker 2006:20; Hocker et al. 2007:479). As a result, the development of the outbreaks has slowed and does not appear to be getting worse either in coverage or pH value (Hocker et al. 2007:479).

In addition to the sulfur problem, many of the epoxy-coated galvanized mild steel bolts, used to replace the rusted away original iron bolts (Figure 10), were corroding in the PEG-treated wood (M. Sandström et al. 2001:69, 88). In the 1960s, when the Conservation Council's recommendation that stainless steel should be used was dismissed, some factors were unforeseen. With time, the increasing acidity has been dissolving the zinc coating, and the corrosion of iron metal has been accelerated by contact with PEG in humid wood (Giulminot et al. 2000; M. Sandström et al. 2003:50-51). As a result, some fifty years later these new bolts display severe corrosion damage and should be replaced (M. Sandström et al. 2001:69, 88; 2003:50). Therefore, a solution is being examined for replacing the corroded ship's bolts with new bolts made of stainless steel, titanium, or carbon fiber. However, this idea has been demonstrated to be more complicated than anticipated and, therefore, it is still under development and research (E. Hocker 2006:19).



Figure 10. Replacing the rusted away original bolts. New epoxy coated galvanized mild steel bolts were inserted into the empty original bolt holes (Courtesy Archives, the Swedish National Maritime Museums).

For the hundreds of wooden objects affected by sulfuric acid, experiments were conducted to evaluate the feasibility of removing the iron corrosion products from the wood (E. Hocker 2006:19). A chelating agent, ethylenediiminobis (2hydroxy-4methyl-phenyl) acetic acid (EDMA), has been demonstrated to effectively remove iron compounds from wood (M. Sandström et al. 2003:50-55; Almkvist et al. 2004). By



eliminating the iron from the wood, the oxidation of the sulfur compound can be drastically slowed or brought to a standstill if RH values are also maintained at 55%. However, the method has some drawbacks, and it is not clear that it could be applied on a large scale. The aqueous solution in which EDMA is applied (Figure 11) is quite alkaline, with pH values from nine to eleven, which can potentially damage the hemicellulose and possibly the lignin of the wood (E. Hocker 2006:19).



Figure 11. Aqueous solution of EDMA. Iron corrosion products being extracted from a wood sample in an EDMA solution (Courtesy Archives, the Swedish National Maritime Museums. Photographer, Stefan Evensen).

Research to understand the complex reactions and the aging of the materials, and to address the challenges that the conservation of the *Vasa* presents is still ongoing in different projects such as *A Future For Vasa* (2008-2011), and will continue for years to come (Elding 2010). The goal, however, is still the same as fifty years ago at the beginning of the *Vasa* conservation project: to ensure the preservation of the *Vasa* for future generations (Barkman 1965:18).

The *Vasa* Museum research program is examining different conservation methods on *Vasa* wood. In 2007, the author contacted the *Vasa* Museum to explore the feasibility of re-treating small artifacts (previously conserved by impregnation with PEG) with alkoxysilanes. In conjunction with the conservators from the *Vasa* Unit, in the *Vasa* Museum, three different wood samples were selected for an extensive research. The research constituted the core of the present MA Thesis at Texas A&M University (TAMU) and, hence, falls outside the main research project initiated by the *Vasa* Museum.

## CHAPTER II

### SILICONES AND CONSERVATION

#### **Silicon Chemistry**

Silicon chemistry was born in 1824 when Jöns Jacob Berzelius, the Swedish chemist who discovered this element (among many other advances for modern chemistry), synthesized silicon tetrachloride. But it was not until a century later when scientists began to understand the importance and potential of this type of compound, resulting in its widespread availability as industrial chemical products around the 1930s (Hardman and Torkelson 1982:20:922; 1989:15:206).

During the first third of the twentieth century, Frederick Kipping pioneered the study of the organic compounds of silicon and invented the term “silicone.” This name was proposed by Kipping under the assumption that these compounds were similar to ketones (Brydson 1982:731; Hardman and Torkelson 1982:20:922; 1989:15:204).

Silicone was originally used to name the synthetic polymers composed of several monomers with a repeating silicon-oxygen (Si-O) backbone with organic groups attached by silicon-carbon (Si-C) bonds (Hardman and Torkelson 1985:1062).

Nowadays, the term silicone has changed, and it is used to refer to the alkoxy silanes. These polymers are also known as silicon esters, or in a more general way, siloxanes (Arkles 1982:20:912-921; 1985:1062).

The polymerization process necessary to the formation of silicone can be summarized as follows: Chlorosilanes or tetraethoxysilane are hydrolyzed obtaining

silanol (SiOH); later, through poly-condensation catalysis it forms polysiloxanes (Figure 12).

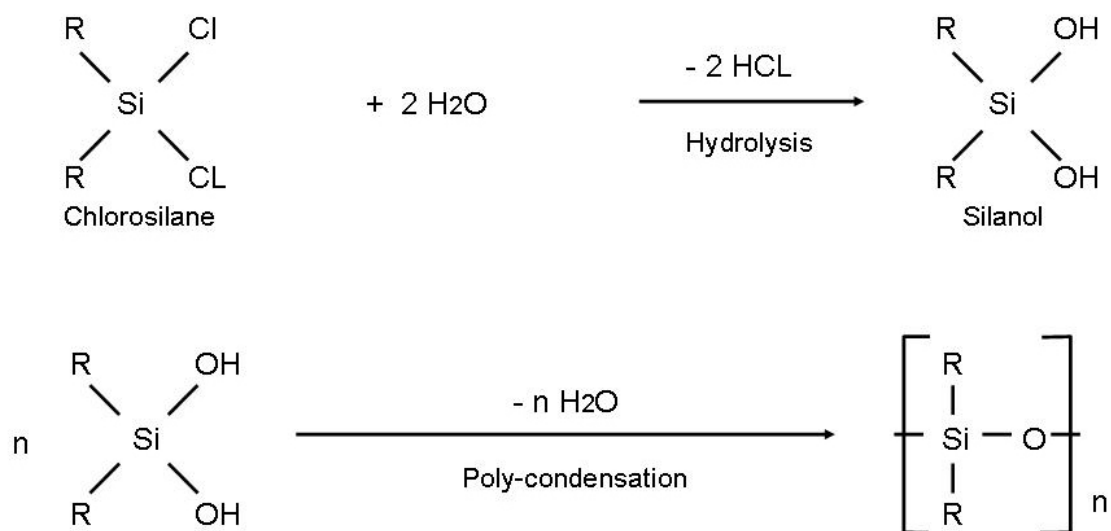


Figure 12. The polymerization process of silicone.

Different types of polymers can be obtained with cross-linked structures and with very different properties and characteristics. To do that, it is necessary to vary the initial monomers of departure and the conditions of the condensation reaction (Matteini and Moles 1989:234).

Industry produces silicones in different formats and for multiple applications. According to their viscosity they are classified in oils, resins, and elastomers. Characterized by their high and permanent resistance to oxidation, silicone oils and resins are used as consolidants in the field of conservation. In the particular case of silicone oils, several types are marketed. The main difference among them is their

viscosity (i.e. molecular weight), which depends on the length of their polymer chains. In addition, the silicone elastomers are frequently used as a molding material for casting. Silicone elastomers, more commonly known as room temperature vulcanizing (RTV) rubbers, are commercialized in two different formats: products of one departure component and products of two departure components (Hardman and Torkelson 1982:20:944-948; 1989:15:273-74).

In one-component products, curing (i.e., hardening) is activated by contact with the atmospheric moisture, as occurs in the case of silicones used as adhesives for commercial applications such as glass. The precursor silicone can be formed by bi-functional or tetra-functional siloxanes (under acidic conditions) or alkoxy silanes (when low pH levels need to be avoided). As we have seen, the polysiloxanes are a product derived from silanol condensation; as the condensation processes progress, the curing of the silicone slows down. This is the reason for the final curing; different energies such as heat, radiation, and chemical catalysts can be and are used (Hardman and Torkelson 1989:15:273-277).

The use of two-components as departure materials is the second approach to the production of silicones. The cure reaction is triggered by mixing the two components, one of which consists of or contains the catalyst. Catalysts include acids and bases: organic soluble salts from lead, cobalt, tin, iron, and other metals as well as other organic compounds from tin. Two-component silicones generally have tri-functional siloxanes as curing agents (i.e., chemical reagent that creates bonds that link one polymer chain to another, promoting a change in the polymers' physical properties). Some silicones use

tetra-functional siloxanes, but this combination implies shorter curing times (Hardman and Torkelson 1989:15:276).

### **Physical and Chemical Properties of Silicones**

Silicones are thermosetting polymers made with highly cross-linked siloxanes that cured form irreversibly materials. In general, silicones are chemically and biologically inert, being very stable against heat, oxidizing agents, and chemical agents. Their physical properties change very little in temperature because of their wide thermal operating range. General purpose silicones have a useful temperature range from -60 °C to 260 °C (Brydson 1982:752; Tomanek 1996:10:7708). Silicone rubber has a flash point of 750 °C and excellent flame retardancy (Tomanek 1996:10:7709). Alkoxysilanes possess excellent thermal stability (Arkles 1985:1062). Some silicon products remain stable up to 200 - 300 °C. The Si- C in methyl silicones breaks at 450 - 500 °C in the absence of air and is susceptible to oxidation near 200 °C (Hardman and Torkelson 1989:15:250-251). Even though silicones are not 100% hydrophobic, they possess a great ability to repel water and form watertight seals. They have an excellent resistance to weathering, oxygen, ozone, ultraviolet light, and gamma radiation (Matteini and Moles 1989:235).

Siloxanes are volatile and have a low viscosity that varies little with changes of temperature. In general, toxicity of siloxanes is very low. However, some types (e.g., tetrametoxysilane) are dangerous to human health (Arkles 1982:20:918-919;

1985:1062). In addition, some curing agents and catalysts can be formulated with high toxicity chemicals (Hardman and Torkelson 1982:20:954-955; 1985:1064).

Some specific properties of the silicones depend on the type of bonds they possess and the nature of their radical groups. The silicon-oxygen (Si-O) bond (of the backbone) and the silicon-carbon (Si-C) bond (of the attached radical groups) are the two most common types of bonds in silicones. The availability of free d orbitals and the electronegativity of silicon are responsible for the characteristics of the silicon-oxygen (Si-O) bond. This ionic bond is very resistant to homolytic cleavage but susceptible to heterolytic cleavage. The silicon-carbon (Si-C) bond is slightly ionic and may or may not be susceptible to heterolytic cleavage, depending on the substituents of the carbon. In addition, depending on the radical groups, some characteristics may differ: Dimethyl silicones, for example, have a high thermal and oxidative stability (Hardman and Torkelson 1989:15:208-209).

### **The Use of Silicones in Inorganic Material Conservation**

The use of silicon compounds as consolidants for lithic material was suggested for the first time by A.W. von Hoffman in 1861. He recommended the use of “silicic ether” (i.e., a form of tetraethoxysilane) for the conservation of the deteriorated limestone ashlar of London’s Houses of Parliament. However, it was not until the 1920s when these products were easily available in the chemical industry that its use as a consolidant received more attention (Wheeler 2005:1).

Nowadays, silicon polymers are frequently used in the consolidation of lithic material and also for other construction materials such as plastered surfaces or *intonacos*. They are often used by conservators as water repellents in diluted concentrations (Matteini and Moles 1989:235). A thorough description of the history and current use of silicon polymers in consolidation of lithic materials can be found in Wheeler 2005.

The composition and properties of the siloxanes make them a very suitable chemical compound for inorganic conservation purposes. Silica (i.e., silicon dioxide,  $\text{SiO}_2$ ) makes up roughly 90% of the crust of the earth (Falcone 1985:1058), whereas silica (i.e. silicon dioxide,  $\text{SiO}_2$ ) makes up roughly 60% of the crust of the earth (Coyle 1982:20:748). Therefore, analogue composition of siloxanes and lithic materials has been decisive for the spreading of these products as stone consolidants. The use of siloxanes as consolidants is based on four main properties: their low viscosity, their ability of being liquid precursors of silica that is formed through a hydrolysis reaction catalyzed by an acid or a base (e.g., diluted hydrochloric acid, acetic acid, etc.), their ability to form siloxane bonds (i.e., Si-O-Si), and their capacity of three-dimensional crosslink (Wheeler 2005:13-27).

A characteristic necessary to always have in mind is that the silicones, as thermosetting plastics, are polymer materials that irreversibly cure; therefore, they are not reversible consolidants. In addition, when silicon compounds are used for the consolidation of lithic materials, they usually cause saturation and subsequent intensification of the color that does not always satisfy the aesthetic demands in conservation (Matteini and Moles 1989:235; Wheeler 2005:48-52).



The main component of glass is silica. Therefore, silicone and glass are highly compatible, and their adherence is exceptionally good. That is why silicones are commonly and widely used in the construction field as glass adhesives (Matteini and Moles 1989:235). The similarity in the composition of glass and silicone polymers suggests the latter as an extremely suitable consolidant for glass. However, being a non-reversible material is a serious inconvenience in some instances.

### **The Use of Silicones in Organic Material Conservation**

At the end of the 1960s at the University of Heidelberg, Germany, Gunter von Hagens developed a technique to conserve biological specimens: *plastination* (von Hagens 1979). The procedure was originally conceived as a technique to prepare and conserve human cadavers as teaching specimens for practice in anatomy and pathology fields. *Plastination* has proven to be a versatile technique with several possible applications. Over time its use has extended to other disciplines such as zoology, botany, archaeology, and also public entertainment (von Hagens et al. 1987:411-413).

The original Von Hagens's technique was awarded and protected by several international patents ((1977) DBPat 27 10 147; (1978) Brit Pat 1 558 802; (1984) Brit Pat 22 082 041; (1978) Belg Pat 863.949; (1978) RSA Pat 78/1330; (1980) Austr. Pat 360 272; (1980) US Pat 4, 205.059; (1981) US Pat 4, 244, 992; (1981) US Pat 4, 278, 701; (1982) US-Pat 4, 320, 157).

The goal of the technique is to replace the main body fluids with silicone polymers. Substituting tissue water and tissue lipids using a thermosetting polymer, the

natural decay of the specimen can be significantly delayed. The procedure can be carried out with different thermosetting polymers. Silicone oils, epoxy resins, and polyester resins are the most common. Silicone oils are used for preservation of organs or whole specimens when flexibility, opacity, and realism are desired. In contrast, epoxy and polyester resins are used when rigidity or transparency are preferred, such as in the case of body slides (i.e., thin sections of the body in which characteristic morphological internal features, anatomical aspects, spatial distribution of bone and tissues, among others, could be appreciated in detail (von Hagens et al. 1987:411-413).

The *plastination* technique contains four main steps in its procedure: fixation, dehydration and defatting, forced impregnation, and curing. A complete and detailed description of the *plastination* technique can be found in von Hagens (1986).

The substitution of the tissue water, or dehydration, is carried out with ethanol or acetone; the latter being the best option since shrinkage is minimal (i.e., smaller than 10%). Dehydration with acetone is carried out by immersion at a -25 °C temperature inside a refrigerated room, stabilizing the specimen shape. Dehydration can be followed by the elimination and substitution of the tissue lipids. Defatting should be carried out with a second bath of acetone but, in this case, at room temperature (since the melting point temperature of lipids is above the -25 °C employed at the dehydration stage). For *plastination*, acetone is a perfect solvent since it acts as a dehydration agent, defatting agent, and intermediary solvent for the different resins used in the procedure (von Hagens et al. 1987:416-417).

Forced impregnation (i.e., the replacement of intermediary solvents by curable polymers) is the main step of the procedure. It is carried out under vacuum at -25 °C. The process takes advantage of the different volatility of the solvent used for the dehydration (i.e., acetone) and the solution of the polymer used as a consolidant. First, a silicone polymer and a catalyst (i.e., Biodur™ S10 and Biodur™ S3) are blended. When the polymer and catalyst are mixed, the curing reaction starts. However, as long as the mixture is maintained at -25 °C, it will remain sufficiently fluid for at least three months. Then the specimen, saturated with acetone, is placed into the polymer solution. Acetone has a high vapor pressure and a low boiling point (i.e., 56 °C), while the polymer solution has a low vapor pressure and a high boiling point. The impregnation is carried out under a slight vacuum and slowly; because the evaporation of the acetone is progressive, it prevents the contraction (i.e., shrinkage) of the specimen (von Hagens et al. 1987:417-418).

The curing process is carried out by vaporization. The decisive crosslinking curing agent is applied to the specimen in gaseous form. Vaporization curing is carried out in a hermetic chamber using a high volatility fluid (i.e., Biodur™ S6). This fluid creates a sufficiently concentrated gas atmosphere to cure the specimens by saturation and diffusion of the gas into the specimen interior. The surface cures within hours, but diffusion of the gas into the center of the specimen can take weeks. Therefore, to ensure proper curing throughout, the specimen is placed into a sealed container (i.e., a plastic bag) allowing a uniform distribution of the crosslinker and the complete hardening of the polymer (i.e., total polymerization). The curing gas is susceptible to humidity that can

cause white stains. It is advisable, therefore, to put a desiccating material inside the chamber in order to avoid a surface with a white appearance (von Hagens et al. 1987:418).

The specimens conserved by *plastination* retain a resilient, flexible, and extremely realistic appearance. An example of the results that can be obtained by the technique are the successful, but controversial, international exhibitions of Dr. von Hagens' *Bodies*, in which human cadavers conserved with the *plastination* technique are displayed.

### **The Use of Thermosetting Resins in Material Conservation**

The use of thermosetting synthetic resins for the conservation of degraded or waterlogged wood was first researched in the Netherlands by R. A. Munnikendam in the late 1960s. Trying to reduce the long treatment time necessary to consolidate waterlogged wood with polyethylene glycol and also to overcome some disadvantages derived from this treatment, Munnikendam conducted a series of experiments to test the applicability of thermosetting synthetic resins for the conservation of waterlogged wood.

In his first experiment, archaeological waterlogged wooden samples were impregnated with two different resins: methyl methacrylate and 2-hydroxyethyl methacrylate. The samples were then polymerized with gamma rays (Munnikendam 1967). The former synthetic resin tested obtained excellent results, whereas the later synthetic resin tested provided unsatisfactory results. In the following years Munnikendam successfully researched the use of low molecular weight epoxy resins for

the consolidation of decayed polychromed wooden objects (Munnikendam 1972). Finally, Munnikendam continued his experiments in order to improve his previous results in the use of 2-hydroxyethyl methacrylate for the conservation of waterlogged wood (Munnikendam 1973). In this experiment, instead of gamma radiation, Munnikendam used heat to polymerize the synthetic resin. In this experiment, the results were satisfactory and better than the results previously obtained.

Silicone products have also been used in the conservation of materials from archaeological origins. Several extensive tests carried out in the late 1960s demonstrated that tropical woods with more than 0.5% of silica in their composition are practically immune to the marine borers (Wallace and Colleti 1970:15-19). Silica has been found responsible for the natural preservation of wood. Therefore since this discovery, silicones have also been tested as a consolidant for wood.

The pioneering use of organo-silicones for the conservation of archaeological waterlogged wood should be attributed to Natela Yashvili, who in the 1960s conducted a series of experiments to test the applicability of some organo-silicones polymers (Yashvili 1975, 1978). In one of the experiments, several waterlogged archaeological wooden artifacts (e.g., a comb, a cup, and a dish, among others) were excavated in eastern Georgia. The objects, which belonged to the Bedeni culture and dated to the twenty-third to twenty-first century B.C., were consolidated with different organo-silicone polymers (i.e., polymethylphenylsiloxane, polymethylsiloxane, polyphenylsiloxane, polyaminhydrosilane and polycyclosiloxane). The objects were first dehydrated by ethyl alcohol and ether baths. Once the objects were dry, a mixture of

polymer and catalyst was applied by brush, and a vacuum was applied to allow deeper penetration. The final polymerization was carried out with heat at 55-60 °C. The author reported excellent results with natural color, no shrinkage, no cracks, and an easy, fast procedure. In order to verify the properties of the conservation technique, the experiment was completed with a six-month accelerated aging test. In the test, the samples were alternatively subjected to sharp variations of humidity and temperature, obtaining satisfactory results (Yashvili 1978:7:3:5). Although these pioneering experiments lacked detailed procedures and quantifiable results, they have the honor of being the first reported attempt to conserve archaeological wood with organo-silicone polymers.

A few years after the pioneering studies of Yashvili, Henry T. Irwin and Gary Wessen conducted research testing the use of another type of organo-silicones (i.e., Tetra Ethyl Ortho Silicate or TEOS) as a possible consolidant for archaeological waterlogged remains (Irwin and Wenssen 1976). In the proposed TEOS procedure, first the waterlogged wood was chemically dehydrated by progressive substitution of water by acetone. Second, the wood was immersed into a solution of acetone and TEOS. Finally, the wood was extracted from the solution and left to dry at room temperature. After the evaporation of the solvent, TEOS hydrolyzed, forming silicon dioxide (i.e., silica) and resulting in the subsequent deposition of silica (Irwin and Wenssen 1976:49-50). The main advantages of this pioneer method using TEOS were summarized by the authors as follows: a preliminary cleaning of the wood is not necessary, there is very short treatment time, and it is a low cost treatment. In addition, the treated wood was resistant to humidity, fungi, and microorganisms (Irwin and Wenssen 1976:53). However, later

studies demonstrated that the results were poor because wood treated with this method became excessively brittle, and light woods become coated with white silica deposits (Grattan 1982:132; Jespersen 1981:203-207).

In the mid 1990s Vera de la Cruz Baltazar wrote a master's thesis compiling her experiences of applying Dr. von Hagens' *plastination* as a consolidation technique for archaeological bone, waterlogged leather, and waterlogged wood (de la Cruz Baltazar 1996). Her research demonstrated that excellent results can be achieved by applying *plastination* to conserve archaeological artifacts, and further research should be conducted before fully recommended this procedure (de la Cruz Baltazar 1996:108). Some other experiments have been carried out in regard to the use of silicones in conservation of organic materials that come from an archaeological origin at Queen's University, Kingston, Canada (Thorp 1980; Norton 1988).

All these experiments were isolated and conducted on a relatively small scale because few objects were treated and studied. It was not until 1996 when a large-scale study, in which a great spectrum of materials were conserved and analyzed, was carried out by Dr. Wayne C. Smith and Dr. Donny L. Hamilton, professors of the Nautical Archaeology Program (NAP) at TAMU.

### ***La Belle* Shipwreck and Texas A&M University**

In 1995 the Texas Historical Commission located the shipwreck of *La Belle* in the Bay of Matagorda. The vessel, one of a small fleet of four ships under the French Flag and the command of the Sieour of La Salle, was on a mission to explore and

establish a fortified commercial port in the Mississippi River mouth. On a winter morning in 1686, the vessel sunk in the waters of Matagorda Bay with its entire cargo (Bruseth and Turner 2005).

The shipwreck waited, buried under the dense mud of the bay, under anaerobic conditions that preserved the organic material: the hull's wooden timbers, cargo, much of the ship's rigging ropes, the crew's utensils, and many other artifacts. Discoveries such as *La Belle* shipwreck are significant because collections of archaeological objects, complete and so well preserved, are rarely found in terrestrial archaeological sites of similar periods. However, the discovery of a shipwreck in such a good preservation status represents a quite complex conservation challenge, taking into consideration that an assemblage of artifacts encompassing more than a million objects remained within preserved the hull (Bruseth and Turner 2005:82-114).

The Conservation Research Laboratory (CRL) at TAMU is one of the most recognized, world-class conservation laboratories. Its main function is to conserve archaeological material from underwater sites. Inaugurated in 1978, it is directed from its foundation by Dr. Donny L. Hamilton, who has published a conservation manual based on experiences in the laboratory and other previous experiences with waterlogged metal, and later a more extensive manual regarding waterlogged archaeological materials (Hamilton 1976; 1996). The CRL plays an important role inside the NAP at TAMU, and works closely with excavation projects of the Institute of Nautical Archaeology (INA). From its opening, CRL has conserved hundreds of thousands of artifacts coming from numerous underwater archaeological excavations such as the twelfth century B.C.



Uluburun shipwreck found in Turkey (Pulak 1998, 2008), or the seventeenth century A.D. sunken city of Port Royal, Jamaica (Hamilton 2000, 2008:259), and a vast array of other projects.

After the discovery of the shipwreck of *La Belle*, the Texas Historical Commission contracted the conservation of the remains of the ship, as well as its cargo, to the CRL. Soon after the discovery of *La Belle* in 1995, a new laboratory was created out of the CRL to concentrate on researching new techniques to conserve archaeological materials. This new laboratory, the Archaeological Preservation Research Laboratory (APRL), directed by Dr. Wayne C. Smith, focuses on the development of new strategies for the stabilization, consolidation, and conservation of organic materials. Research at APRL has especially been focused on the development and applicability of organo-silicones chemistry, its polymers, and its applications in the field of conservation. These investigations were carried out jointly with Dr. Jerome M. Klosowski from the Dow Corning™ Corporation, manufacturer of chemical materials among which silicone oils are included. As a result of this joint research by Dr. Klosowski, Dr. Smith, and Dr. Hamilton, five United States Patents were awarded over the time ((1998) US Pat 5, 789.087; (2000) US Pat 6, 020, 027; (2002) US Pat 6, 432, 553; (2004) US-Pat 6, 835, 411; (2005) US Pat 6, 881, 435). Despite the protection of the patents, the authors permit the use of these procedures to non-profit applications, such as conservation by museums.

The more than one million objects to conserve from *La Belle* shipwreck and the parallel research developed by the APRL created a *momentum* that made possible, for

the first time, the development of a large-scale case study regarding the applicability of organo-silicones and their use in archaeological material conservation.

### **Silicone Oil Treatment**

Since 1997 the APRL has investigated multiple applications of silicone oils in the field of archaeological materials conservation. Among them, organic materials such as wood, leather, textiles, and rope; inorganic materials such as glass; and mixed materials such as bone, antler, and ivory. These experiments provided the foundation of knowledge from which different procedures with alkoxysilanes have been developed for conserving archaeological materials (Smith 2003, 2008). Several reports in relation to each one of the experiments can be found in Smith (2003) as well APRL's website (Smith 2008).

The silicone oil treatment, overall, is quite similar to the one developed by von Hagens (i.e., *plastination*) but with some substantial differences summarized in the following Table 1.

Table 1. Main differences between *plastination* and silicone oil.

	<i>Plastination</i>	Silicone oil
Temperature at which the procedure is perform	-25 °C	Room temperature
Mixture used as consolidant	Polymer + Catalyst	Polymer + Crosslinker
Completion of the polymerization process	By vaporization of a Crosslinker	By vaporization of a Catalyst

The von Hagens procedure uses a polymer and a catalyst to impregnate the specimen followed by the vaporization of a crosslinker to complete the polymerization process. Since the mix of polymer and catalyst is highly reactive, *plastination* has to be conducted at -25 °C in order to slow down the reaction. Whereas the silicone oil treatment uses a mix of polymer and crosslinker to impregnate the artifact, followed by the vaporization of a catalyst to finalize the polymerization process. The lack of reactivity in between the polymer and the crosslinker allows the procedure to be carried out at room temperature and keeps the mixture sufficiently fluid for years.

Due to the toxicity of the material used in these procedures (i.e., solvents, silicone oils, crossliker, and catalysts), safety is very important; product literature and Material Safety Data Sheets should always be consulted before use. It is recommended that the process be executed with personal protection; at a minimum, gloves, eye protection, and respirators should be worn, and, if possible, work should be conducted in a ventilated area under a fume hood.

The silicone oil method uses a mixture of polymer and crosslinker to impregnate and consolidate artifacts, followed by the vaporization of a catalyst to finalize the polymerization process. This method used by the CRL can be summarized in five fundamental steps: desalination, dehydration, forced impregnation, cleaning, and catalysis.

### ***Desalination***

In this study this step was not necessary because it was previously conducted. Yet it is described as part of the general CRL method procedure where the waterlogged wood is recovered from a marine or saline environment. Objects are first desalinated in sequential water baths of tap water, reverse osmosis water, and deionized (DI) water until reaching low concentration levels of salts (e.g., less than 25-30 ppm of chloride). The desalination process is performed by the diffusion of salt through the exchange of sequential water baths of lower salt concentration. Once the bulk of the soluble salts are removed from the object, the solvent dehydration process begins.

### ***Solvent Dehydration***

Water extraction from the samples, or dehydration, is carried out by progressive solvent dehydration. Two solvents are used: ethanol and acetone. Solvent dehydration consists of replacing the water gradually by using more polar solvents in a progressive sequence. The process starts by taking the object through sequential baths of water/ethanol, increasing the ethanol with each bath until reaching 100% ethanol. The

ethanol is then replaced with sequential baths of increasing acetone concentration until 100% acetone is reached. Depending on the sample the increases in percentage of ethanol and acetone range from 5% to 25%.

For example, the initial solution, or first vat, is made of 75% deionized water and 25% ethanol. The second vat is made of 50% deionized water and 50% ethanol. The third vat is made of 25% deionized water and 75% ethanol. The fourth vat contains a solution of 100% ethanol. This process is repeated with another four vats and increments of 25%, but in this case, the acetone concentration is increased until it reaches 100% acetone concentration. Finally, an extra vat with 100% fresh acetone is used to complete the dehydration process. The process requires a sequence of nine baths that vary in 25% increments from the initial solution to the final bath.

Objects that are to be dehydrated remain for variable length of a specific time in the different dehydration vats. The length of time for dehydration is determined on a case-by-case basis based on its material nature, preservation status, and size. As a general rule, objects remain a minimum of 24 hours in each vat of the dehydration process. One important aspect of the dehydration process is penetration of the solvent through the porous material's physical structure. Penetration of the solvent occurs by capillary action in which surface tension and density of the solvent are the most important factors. However, in the case of relatively small objects, the penetration of the solvent into the material's physical structure can be speeded up with the use of low vacuum through a suction pump.

### ***Forced Impregnation***

Prior to the forced impregnation, silicone oil that possesses the most convenient molecular weight for the object to be conserved (i.e., with an appropriate viscosity) must be selected. In this decision, the nature of the artifact, porosity of the material, and degree of preservation, among other factors, must be considered. As standardized procedure in the CRL, the method uses a mixture of the most desired molecular weight silicone oil and a 20% (by volume) of crosslinker.

The silicone oils commonly used in the method are dimethyl siloxane hydroxyl-terminated polymers. These silicones are produced by the chemical industry in many different types and different viscosities that all are applicable for archaeological conservation. The CRL utilizes non-commercialized polymers (i.e., SFD-1 silicone oil) manufactured by Dow Corning™ Corporation, which donates the polymers. However, polymers with similar characteristics to those used by the CRL (also made by Dow Corning™) could be purchased under the brand name of DC200® Fluid, which recently changed its commercial name to Xiameter® PMX-200 Silicone Fluid. Nonetheless, the CAS registry number of the PDMS polymer is 70131-67-8 (Grant 1996:10:7699).

Two main polymers are used in the CRL that have similar composition, whereas their viscosity differs: a low viscosity oil SFD-1 (~75 cSt) and a medium viscosity oil SFD-5 (13,500 cSt). The combination of these two oils provides a wide range of mixtures with different viscosities that allows the impregnation of diverse materials according to its specific necessities. In general practice, SFD-1 is the most versatile and is used most often. The crosslinker used in the CRL is methyltrimethoxysilane (MTMS),

commercialized with the name DC® Z-6070 SILANE (1 cSt), which recently changed its commercial name to Xiameter® OFS-6070 Silane. However, the CAS registry number of MTMS is 1185-55-3 (Hardman and Torkelson 1982:20:914).

Forced impregnation is carried out by transferring the object coming from the last vat of 100% fresh acetone to a recipient container with the proper mixture of silicone oil and crosslinker (i.e. SFD-1 + 20% Z-6070). The object must be transferred quickly while it remains soaked in acetone in order to avoid undesired evaporation of the acetone and subsequent structural collapse. The object should remain immersed in the polymer solution during the forced impregnation. Throughout the exchange of acetone and polymer mixture, the object usually has a tendency to float due to the high viscosity of the silicone oil. To assure the immersion of the object in the mixture, a mesh made of plastic or aluminum can be used in combination with a weight. Once the object is kept immersed in the silicone oil mixture, the container is moved to a vacuum chamber to *force* its impregnation and to facilitate the acetone/polymer exchange.

If the object is small in size, glass desiccators can be used as a vacuum chamber. The pressure applied is just enough to facilitate the process (i.e., when small bubbles appear from the object), as the acetone vaporizes under vacuum around approximately 15 mm Hg and never more than 25 mm Hg. By applying vacuum, liquid acetone boils and evaporates to a gaseous state. In order to avoid uncontrolled boiling of the acetone, which could possibly damage the cellular structure of the samples, the vacuum is increased in progressive steps until the proper vacuum level is reached. The vacuum is also gradually decreased with the purpose of avoiding damaging the structure of the

sample due to an uncontrolled release of pressure. In this process, the acetone vaporizes under vacuum coming out of the wood. As the acetone leaves the cells it facilitates the penetration of the oil into the cells. Then when the vacuum is lost, the atmospheric pressure forces the oil into the wood. The wood is then impregnated with the silicone oil/crosslinker polymer solution. Finally, the object is left in the polymer solution at ambient pressure for a minimum period of 24 hours.

### *Cleaning*

After completing the acetone/polymer exchange, the silicone excess (i.e., free-flowing polymer) must be extracted from the object. The removal of this non-essential polymer is a very important step in obtaining satisfactory results. If the excess of oil is left in the object, a thick rubberized layer of silicone will be left on the surfaces. The cleaning of the object is addressed by several processes. First the object is placed on a mesh to allow the nonessential polymer to drain for at least 24 hours. It is important to note the silicone oil recovered can be recycled and reused for conservation of other objects similar in nature. If necessary, once the object is drained it can be immersed in crosslinker (i.e., MTMS) for periods up to 30 minutes. This step will help to dissolve, remove, and rinse the excess nonessential silicone oil. Finally, the object is cleaned and dried by blotting its surface with nonabrasive tools such as soft toothbrushes, paint brushes, cotton-tipped applicators, lint-free cloths, and paper towels.



### *Catalysis*

As the final step, the silicone oil retained within the object is cured by vapor deposition catalysis. In the CRL, two possible catalysts are used: TPT Titanate or DBTDA. The former is a chemical reactive which is composed of tetra iso propyl titanate (99%) and isopropylic alcohol (1%); this product is commercialized as Tyzor® by Dupont® laboratories. The latter is a tin derivate: dibutyltin diacetate. In vapor deposition catalysis, the object must be placed in a sealed plastic bag along with a container that holds several milliliters of catalyst for a minimum period of 24 hours. Alternatively, a small piece of wadded paper towel can be saturated with catalyst and placed in the container. The catalysis process must be repeated, replacing the catalyst with a fresh one, at least three more times in periods of 24/48 hours each. However, it is recommended to leave the object in the last catalysis step for a period of one week to assure a complete catalysis. Once the object has been totally catalyzed, it is advisable to eliminate the residual vapors in the object from the catalyst. Thus, the object is placed into a fume hood for at least 24 hours to remove all possible residual vapors.

### CHAPTER III

#### OBJECTIVES AND RESEARCH PLAN

The main objective, or purpose, of this research was to explore the feasibility of re-treating artifacts (previously conserved by impregnation with PEG) with alkoxysilanes. Three different re-conservation procedures were tested focusing on small, organic, wood samples from the *Vasa*. The three re-conservation procedures were: (1) the method used by the Conservation Research Laboratory (CRL) using silicone oil and a crosslinker; (2) a MTMS treatment developed by Dr. Wayne Smith; and (3) a MTMS treatment variation developed by the author. The results of each re-conservation procedure were compared, on each sample, with the previous conservation treatment.

The study was part of a *Vasa* Museum research program to examine different conservation methods on *Vasa* wood, including silicon oil (i.e., alkoxysilanes). In conjunction with the conservators from the *Vasa* Unit in the *Vasa* Museum, three different wood samples were selected for an extensive research. The research constituted the core of this thesis at TAMU and, hence, falls outside the main research project initiated by the *Vasa* Museum.

In any study, experiment, or scientific research the first step is to establish a plan with a timeline, which is the “research plan.” This research plan should include each of the phases and/or steps necessary to accomplish the goals of the experiment. In the research plan, each phase should be described explaining several aspects as: its order in the overall scheme, purpose, methodology, and expected results.

Therefore, in June 2007 the author together with Emma Hocker and Malin Sahlstedt, members of the Conservation Unit of the *Vasa* Museum, decided which steps would be necessary to accomplish the goals of this research. A complete research plan was developed that established three main phases and their timelines. Each phase serves to its own purpose, including the different steps necessary to accomplish the research's goals. The research plan, specifically designed for this study, is presented as follows.

### **PHASE 1: *Vasa* Museum (June 2007)**

#### ***Samples Selection***

Objective: To select appropriate samples for the purpose of this research. Three different wood samples were selected with the intent that all of them came from the *Vasa's* original seventeenth century pine.

1. Sample of untreated waterlogged pine wood
2. Sample of conserved pine wood with the 1960s PEG treatment
3. Sample of 1960s PEG treatment conserved pine wood, re-treated for extraction of ferric compounds with the chelate agent EDMA (i.e., Ethylenediiminobis (2hydroxy-4methyl-phenyl) acetic acid)

All three samples were re-conserved. In addition, the untreated waterlogged wood served as control. The original PEG conserved wood was used to record the extraction process of PEG. The EDMA sample, in which ferric compounds were extracted (and subsequently PEG since the process was done in an aqueous solution), served as a control and also was re-conserved.

### ***Documentation of the Samples***

Objective: The basic physical characteristics of each sample were recorded by means of photographs and linear and weight measurements, before taking the samples to TAMU from the *Vasa* Museum.

### ***Packing and Shipping Samples***

Objective: The samples were packed to prevent any alterations or damage to them while intransit from the *Vasa* Museum to TAMU.

Dry samples: These samples were covered and packed with chemically inert packing materials such as polyethylene foam and bubble plastic. The protected samples were then placed in Ziploc® plastic bags and finally, sealed in a polyethylene watertight container.

Waterlogged samples were packed in sealed containers that maintained the humidity level. The waterlogged samples were wrapped using polyether foam that absorbs and retains water. Deionized water was used. A biocide solution (i.e., 2% boric acid solution and borax 7:3) was added in order to prevent biological development. The wrap samples were individually placed into plastic bags and sealed in watertight polyethylene containers.

All plastic bags and containers were labeled with the identifying reference number of each sample. Finally, the containers of each group of samples (dry and waterlogged) were protected with packing materials such as foam or bubble plastic and placed in a rigid cardboard box.

## PHASE 2: Texas A&M University (August 2007-May 2008)

### *Pre-Treatment Documentation*

Objective: To record the physical and chemical characteristics of every sample before the re-conservation process (Table 2).

Documentation: Before any intervention and after each phase, a thorough examination of the samples was conducted with an appropriate record system. These analyses, and the reports derived from them, were able identify the physical and chemical characteristics of each sample, its structures, materials, and condition.

Table 2. Proposed pre-treatment documentation.

Sample Identification	Record the samples	Sample Analysis
<ul style="list-style-type: none"> <li>• Nature</li> <li>• Type of wood</li> </ul>	<ul style="list-style-type: none"> <li>• Photographs</li> <li>• Color (Munsel chart)</li> <li>• Linear &amp; weight Measurements</li> <li>• Volume (3D Scan)</li> </ul>	<ul style="list-style-type: none"> <li>• EDS</li> <li>• XPS</li> <li>• Raman-FTIR</li> </ul>

Physical analysis: Different techniques were used to measure and record selected physical characteristics of the samples in each phase of the research. The use of linear measurements and contour tracing complemented with a 3D scanner provided the linear and volumetric measurements necessary to control possible shrinkage or swelling of the samples. Munsel color designations were used in order to determine the color alterations of the samples.

Chemical analysis: Three non-destructive spectrographic types of analysis (i.e., EDS, XPS, and Raman-FTIR) were conducted throughout different phases of the experiment. The objective was to record the nature of foreign elements and their quantities in the samples. The analytical techniques used were complementary, and the sum of them provided an accurate analysis of the substances present in the samples.

### ***Extraction of Ferric Compounds and PEG***

Objective: To extract the ferric compounds in order to re-serve the samples. Ferric compounds were previously extracted at the *Vasa* Museum with the chelate agent EDTA (Almkvist et al. 2004). The EDTA sample used for this research came from a sample where extraction of ferric compound was previously conducted at the *Vasa* Museum. Thus, the author conducted no extraction of ferric compound or PEG for the EDTA sample. Since the ferric compounds extraction is conducted in an aqueous solution, the PEG from the 1960s conservation treatment is also irretrievably removed.

In the PEG sample, the extraction of original 1960s PEG was achieved by diffusing the PEG out of the wood (through reverse osmosis) by immersing the sample in deionized water at 60 °C in a vented warming oven. The process was monitored and recorded. The sample's weight loss was measured with a digital scale.

### ***Post-Extraction Documentation***

Objective: To record physical and chemical changes that the samples could experienced after the PEG extraction process. This was one of the most important phases of the research because important information was gathered.

- Percentage of PEG in the samples
- Measurement of effectiveness and rate of PEG extraction
- Shrinkage or swelling of the samples after treatment

### ***Re-Conservation Treatment***

Objective: To re-serve the samples with two different alkoxy silanes (i.e., MTMS and silicone oil) and three different re-conservation procedures (Table 3).

Table 3. Main processes of the proposed re-conservation treatments.

Silicone oil method	Smith's MTMS method	Author's MTMS method
<ul style="list-style-type: none"> <li>• Solvent Dehydration</li> <li>• Impregnation with Silicone oil + MTMS</li> <li>• Remove nonessential polymer</li> <li>• Polymerization by vapor catalysis</li> </ul>	<ul style="list-style-type: none"> <li>• Immerse the sample in MTMS at 70 °C</li> <li>• PEG removal by diffusion</li> <li>• Controlled Air-drying</li> <li>• Polymerization by vapor catalysis</li> </ul>	<ul style="list-style-type: none"> <li>• PEG removal by reverse osmosis in DI water at 60 °C.</li> <li>• Solvent Dehydration</li> <li>• Impregnation with MTMS</li> <li>• Polymerization by vapor catalysis</li> </ul>

### ***Silicone Oil Method***

This procedure was previously described in detail in Chapter II of this thesis and also in Smith (2003:21-30).

### ***MTMS Method***

This procedure developed by Dr. Wayne Smith is described in detail in elsewhere (1998; 2003:30-45). The process consists of immersing a previously PEG-treated sample into a container (i.e., beaker) with MTMS. The container is covered tightly with aluminum foil to prevent the rapid evaporation of the silane. The container with the immersed sample is then placed into a vented warming oven for 24 hours at 70 °C. The container is removed from the oven and allowed to cool to room temperature. The wood sample is removed from the container and dried at room temperature.

According with Smith, during this re-treatment, unbound, free-flowing PEG from the cells of wood sample is removed from the wood. In the aqueous environment of the PEG-treated wood, the MTMS displaced free-flowing PEG within the cell voids of the wood, hydrolyzing to form methyl silane polymers (Smith 2003:31).

### ***Author's MTMS Method***

This procedure is described in detail in Chapter VII of this thesis. The PEG from the 1960s original conservation process is removed, diffusing the PEG out of the wood (through reverse osmosis) by immersing the sample in deionized water at 60 °C in a vented warming oven. Then the sample is dehydrated by taking it through several baths



of organic solvents (i.e.. solvent dehydration). The sample is immersed in MTMS at room temperature under a minimal amount of vacuum. The sample is dried out at room temperature. Complete polymerization is achieved over time by vapor catalysis.

#### ***Expected Results Silicone Oil Method***

The re-treated sample should present a dry, non-sticky surface with good texture and color close to the original wood. The sample should present minimum shrinkage and no swelling after the re-treatment. The sample should recover elasticity and strength. Additionally, due to the nature of the polymer used as the consolidant, the sample should be less affected by environmental conditions such as ultraviolet light and variations in temperature and/or relative humidity.

#### ***Expected Results MTMS Method***

The re-treated sample will lose weight (due to the loss of unbound PEG). It should present a dry, non-sticky surface, recovering texture and color closer to the original. The sample should present minimum shrinkage and no swelling after re-treatment. The sample should recover elasticity and strength. Additionally, due to the nature of the polymer used as consolidant, the sample should be less affected by environmental conditions such as ultraviolet light and variations in temperature and/or relative humidity.

### ***Expected Results Author's MTMS Method***

The re-treated sample loses weight (due to the loss of PEG). It should present a dry, non-sticky surface recovering texture and color closer to the original. The sample should present minimum shrinkage and no swelling after the re-treatment. The sample should recover elasticity and strength. Additionally, due to the nature of the polymer used as consolidant, the sample should be less affected by environmental conditions such as ultraviolet light and variations in temperature and/or relative humidity.

### ***Post-Treatment Documentation***

Objective: To record all physical and chemical changes that the samples could experienced after the different re-conservation processes (Table 4). This was one of the most significant phases of the research because important information was gathered.

Table 4. Proposed post-treatment documentation.

Record the samples	Sample Analysis
<ul style="list-style-type: none"> <li>• Photographs</li> <li>• Color (Munsel chart)</li> <li>• Linear &amp; weight Measurements</li> <li>• Volume (3D Scan)</li> </ul>	<ul style="list-style-type: none"> <li>• EDS</li> <li>• XPS</li> <li>• Raman-FTIR</li> </ul>

### ***Conclusions***

All of the data gathered and the conclusions reached after its examination were compiled in a research preliminary report.

### **PHASE 3: *Vasa* Museum (June 2008)**

The preliminary conclusions were presented in a report supported by a presentation to the *Vasa* authorities and conservation team. After the presentation at the *Vasa* Museum, the final complete compilation of the data gathered and the final interpretation of the results were compiled for this thesis.

CHAPTER IV  
PRE-TREATMENT DOCUMENTATION

**Sample's Measurements of the *Vasa* Research**

**“Waterlogged Sample” (WS)**

Untreated waterlogged wood (pine?). *Vasa* Museum # 24248 (Figure 13). Total weight: 122.11 gr.

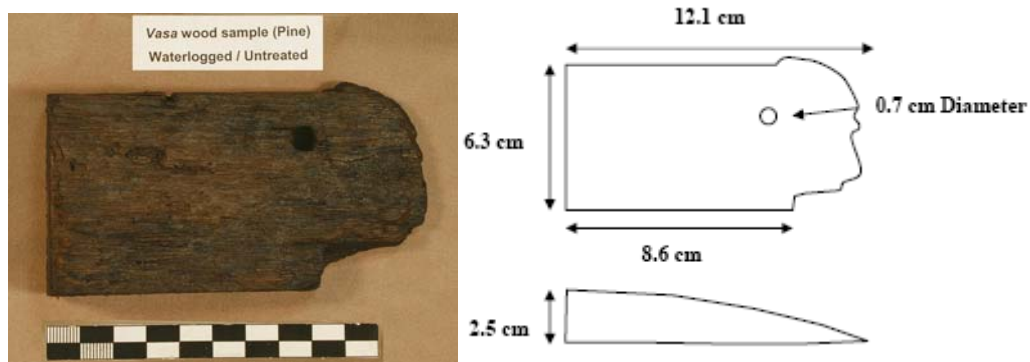


Figure 13. Photo and dimensions of the waterlogged wood sample.

This was the first *Vasa* Museum artifact (number 24248) selected for the pilot study as the untreated wood sample. According to the *Vasa* Museum archives, the artifact was recovered from the seabed of Stockholm Bay on February 2, 1988, in a routine survey of the *Vasa* shipwreck underwater archaeological site. Since then, the artifact was kept in DI water in the *Vasa* Museum storage until this pilot study. The

nature of the wood was not specified in the archives, but at the time of the selection (i.e., June 2007) without microscopic analysis, the author believed it was pine.

**“EDMA Sample” (ES)**

EDMA treated wood sample (pine). *Vasa* Museum # 17396 (Figure 14). Total weight: 356.60 gr.

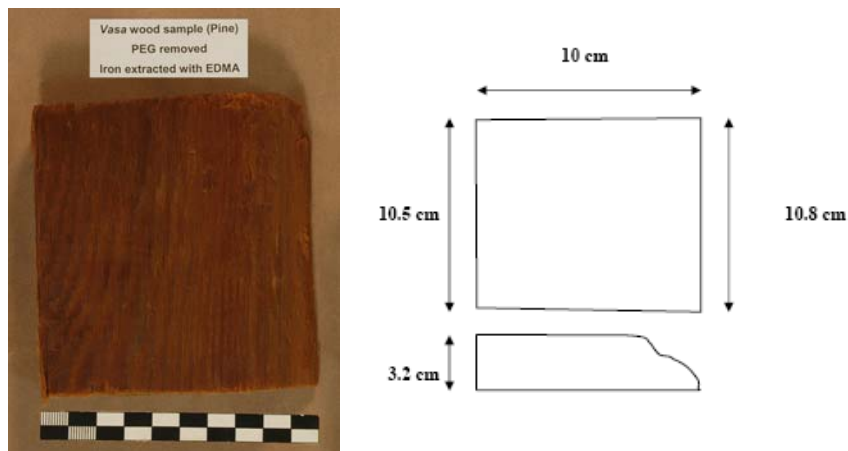


Figure 14. Photo and dimensions of the EDMA treated wood sample.

This is the second *Vasa* Museum artifact (number 17396) selected for the pilot study as the EDMA treated wood sample. This sample was originally part of a bigger artifact. According to the *Vasa* Museum archives, the artifact was recovered from the seabed of Stockholm Bay on August 24, 1961, in the recovery works of the *Vasa*. The artifact was conserved by total impregnation of PEG 4000 in the 1960s (Barkman

1965:8-13; 1975:71-82; 1976:50-53; Håfors 1993:52) and has been kept since then in the *Vasa* Museum storage. From September 2002 to June 2005 the artifact was treated at the Beckholmen Laboratory (part of the *Vasa* Museum) by aqueous solution of EDMA in order to extract iron compounds dissolved into the wood (Almkvist et al. 2004:203-211). According with the *Vasa* Museum archives, the wood is pine. For this pilot study, the EDMA sample was cut from the larger artifact in June 2007.

### “PEG Sample” (PE)

1960s original PEG treated wood (pine). *Vasa* Museum # 13473 (Figure 15).

Total weight: 302.92 gr.

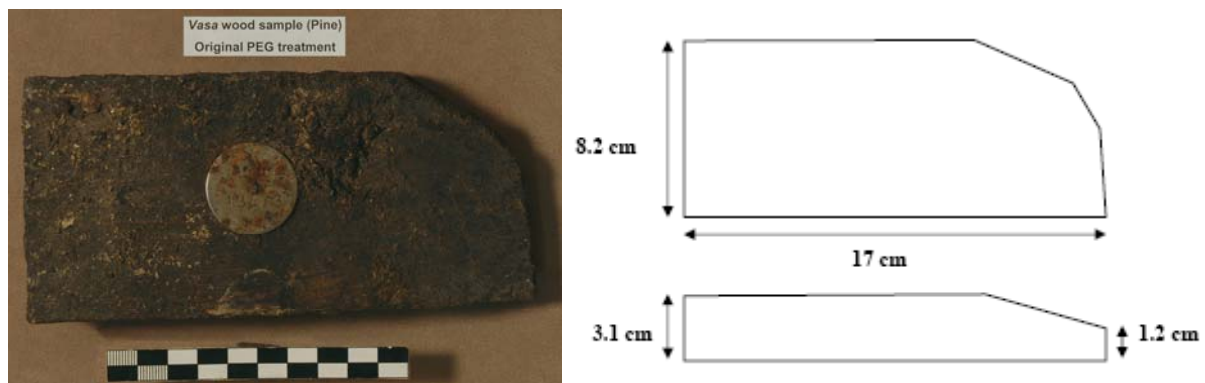


Figure 15. Photo and dimensions of the PEG treated wood sample.

The third *Vasa* Museum artifact (number 13473) was selected for the pilot study as an example of PEG-treated wood. According to the *Vasa* Museum archives, the

artifact was recovered from the seabed of Stockholm Bay on July 7, 1961, during the recovery works of the *Vasa*. The artifact was conserved by total impregnation of PEG 4000 from September 1964 to November 1965 (Barkman 1965:8-13; 1975:71-82; 1976:50-53; Håfors 1993:52). Since the original conservation procedure the artifact had been kept in the *Vasa* Museum storage until the occasion of this pilot study.

## CHAPTER V

### EXPERIMENT DESIGN

#### ***Vasa* Research Samples' Sub-Divisions**

The main objective of this research was to test three re-conservation procedures using alkoxysilanes. Therefore, the three original samples had to be divided in several sub-samples in order to test the different re-conservation procedures (Figure 16).

The sub-samples from each of the samples served three different purposes: control, analysis, and re-treatment. Reserving and keeping sub-samples as controls of every step of the process allows anyone to re-analyze and double-check the samples, at any stage of the experiment or after the experiments are completed.



Figure 16. Wood samples being divided. Glen Grieco using a band saw for dividing the samples.



### *Sub-Divisions and Purpose of the “Waterlogged sample” (WS)*

#### Group 1

Control and analysis of the original conditions of the waterlogged wood (Figure 17).

WS1 – Sub-sample used for pre-treatment analysis.

WS2 – Sub-sample reserved as control of the original waterlogged status of the wood.

WS3 – Sub-sample reserved as control of the original waterlogged status of the wood.



Figure 17. Two images of the waterlogged sample (WS). Left, drawing of the approximate location of the sub-divisions (dotted line); right, photography of WS during the process of being cut into several sub-samples.

## Group 2

Conservation of the sub-sample WS4 with silicone oil.

WS4 – Sub-sample reserved as control of the silicone oil treatment.

WS4.a – Sub-sample used for post-treatment analysis.

## ***Sub-Divisions and Purpose of the “EDMA Sample” (ES)***

### Group 1

Control and analysis of the original conditions of the PEG-extracted and EDMA-treated sample (Figure 18).

ES1 - Sub-sample used for pre-treatment analysis.

ES2 - Sub-sample reserved as control of the original conditions of the PEG-extracted and EDMA-treated sample.

ES3 - Sub-sample re-conserved with MTMS.

ES3.a - Sub-sample used for post-treatment analysis.

### Group 2

Re-conservation of the sub-sample ES4 with silicone oil.

ES4 – Sub-sample reserved as control of the silicone oil treatment.

ES4.a – Sub-sample used for post-treatment analysis.

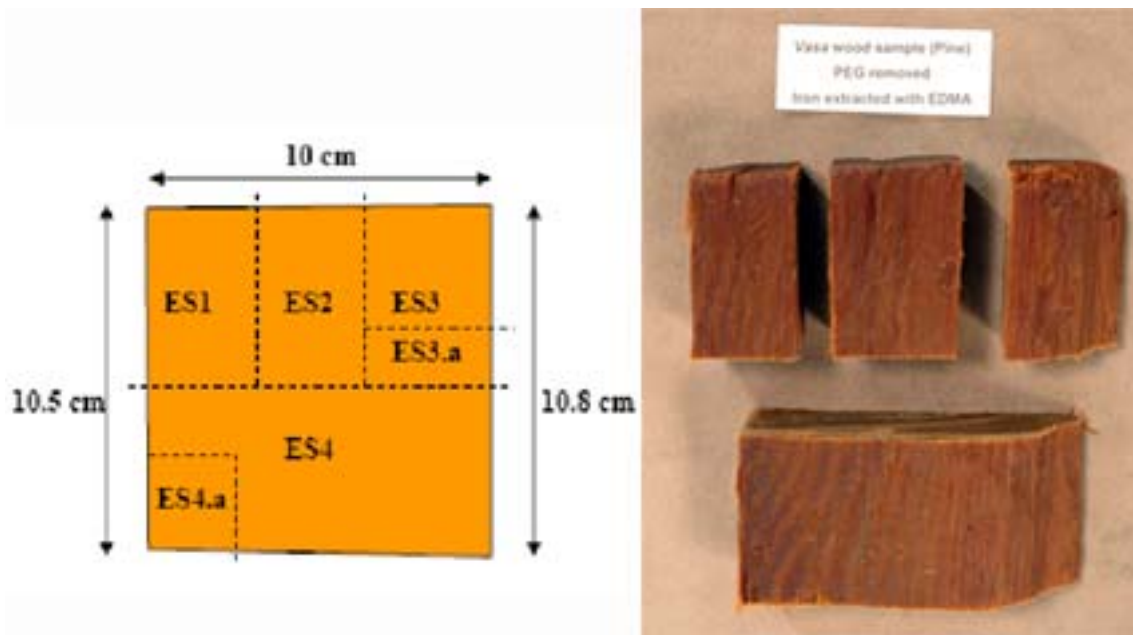


Figure 18. Two images of the EDMA sample (ES). Left, drawing of the approximate location of the sub-divisions (dotted line); right, photography of ES during the process of being cut into several sub-samples.

### ***Sub-Divisions and Purpose of the “PEG Sample” (PS)***

#### **Group 1**

Control and analysis of the original conditions (original PEG treatment) (Figure 19).

PS1 – Sub-sample used for pre-treatment analysis.

PS2 – Sub-sample reserved as control of the original PEG treatment.

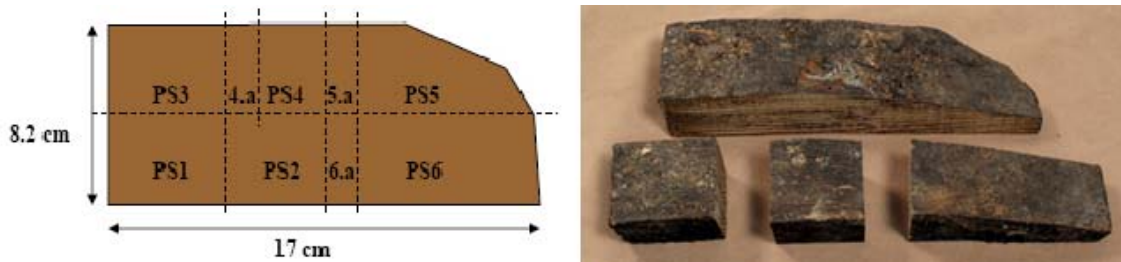


Figure 19. Two images of the PEG sample (PS). Left, drawing of the approximate location of the sub-divisions (dotted line); right, photography of PS during the process of being cut into several sub-samples.

### Group 2

Re-conservation of the sub-samples PS3, PS4, and PS5 with MTMS and silicone oil.

PS3 – Sub-sample reserved as control of the PEG extraction.

PS4 – Sub-sample reserved as control of MTMS treatment.

PS4.a – Sub-sample used for post-treatment analysis.

PS5 – Sub-sample reserved as control of the silicone oil re-treatment.

PS5.a – Sub-sample used for post-treatment analysis.

### Group 3

Re-conservation of the sub-sample PS6: Re-treatment with MTMS method.

PS6 – Sub-sample reserved as control of the MTMS re-treatment.

PS6.a – Sub-sample used for post-treatment analysis.

### **Preparation for Analysis**

Critical for the success of this research was the documentation of foreign chemical substances present in the wood samples before and after the re-conservation process. Thus, chemical analyses were made in order to measure the presence and distribution of two particular elements (i.e., iron and sulfur) before the samples went through re-conservation. Also, analyses were made to document the presence of the two conservation substances (i.e., PEG and alkoxy silanes) related to this study.

The primary goal of the chemical analysis was to identify the presence of iron compounds and sulfur salts. Second, but not less important, was to attempt to record the distribution and penetration of these two substances. Therefore, each of the samples selected for chemical analysis was sliced into three sections. By slicing the samples in three levels or sections it is possible to obtain a three-dimensional map of the distribution and penetration of these chemical elements. The sub-samples were prepared gently by hand, slicing the three sections or levels with the aid of a Japanese saw (Figure 20).

Prior slicing the samples, they were marked with a small incision in one of the external surfaces, which always corresponded to the radial or tangential surface of the wood. The purpose of the incision was to easily identify each surface of the sample and the relative position of every spot selected for analysis (Figure 21).



Figure 20. Two images of the slicing process. Left, Christopher Atkinson slicing one of the sub-samples with a Japanese saw; right, the resulting slices of EDMA sub-sample (three on top) and waterlogged sub-sample (three on the bottom).

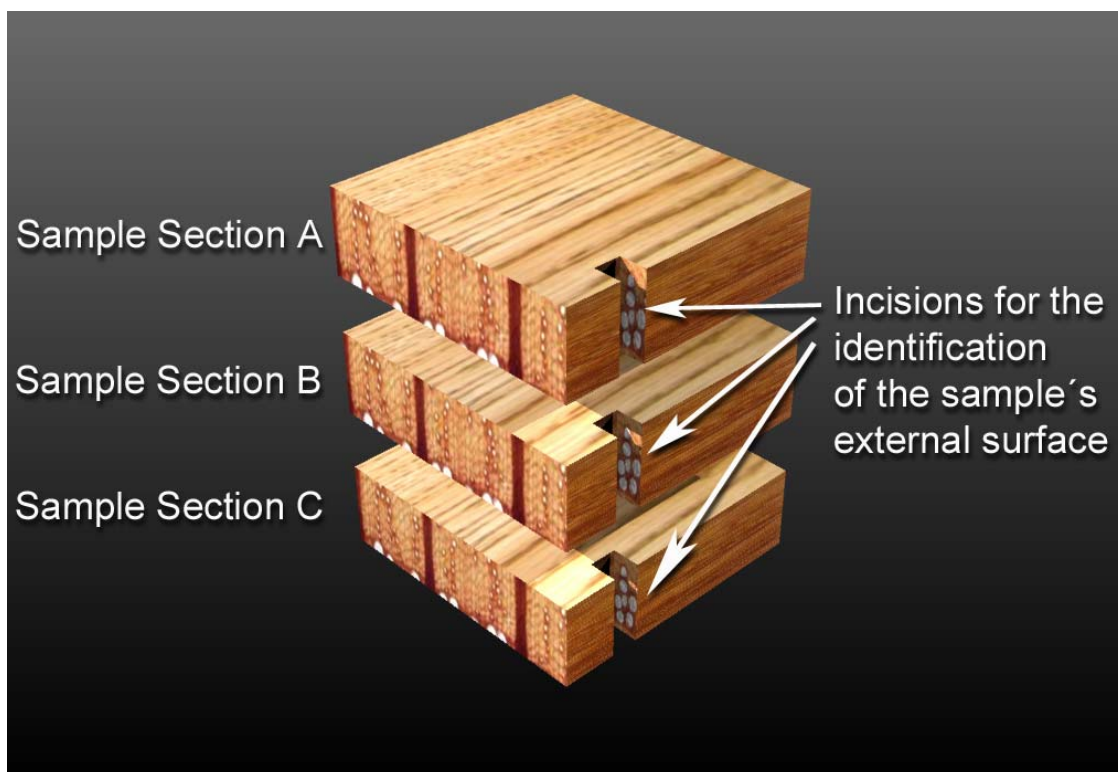


Figure 21. Sections of the samples. 3D reconstruction of how each sample was marked with a small incision and sliced into three sections.

In order to obtain a three-dimensional map of the distribution and penetration of the chemical elements from the resulting three sections, of each sample, three spots of each section were analyzed. Therefore, on every sample nine spots were selected for chemical analysis. The three selected spots to be analyzed were located on each superior upper surface of each section of the sample. In this way, the external and the internal structure of the wood sample were analyzed. The surface of section “A” corresponds to an external surface of the wood sample. The surfaces of the sections “B” and “C” correspond to two different internal planes of the wood sample. Additionally, the three spots run from the external corner of the sample to the internal corner of the sample. This configuration was designed with the purpose of obtaining a three-dimensional map of the distribution and penetration of the chemical elements within the wood before and after treatment. The same procedure was followed with each of samples selected for chemical analysis.

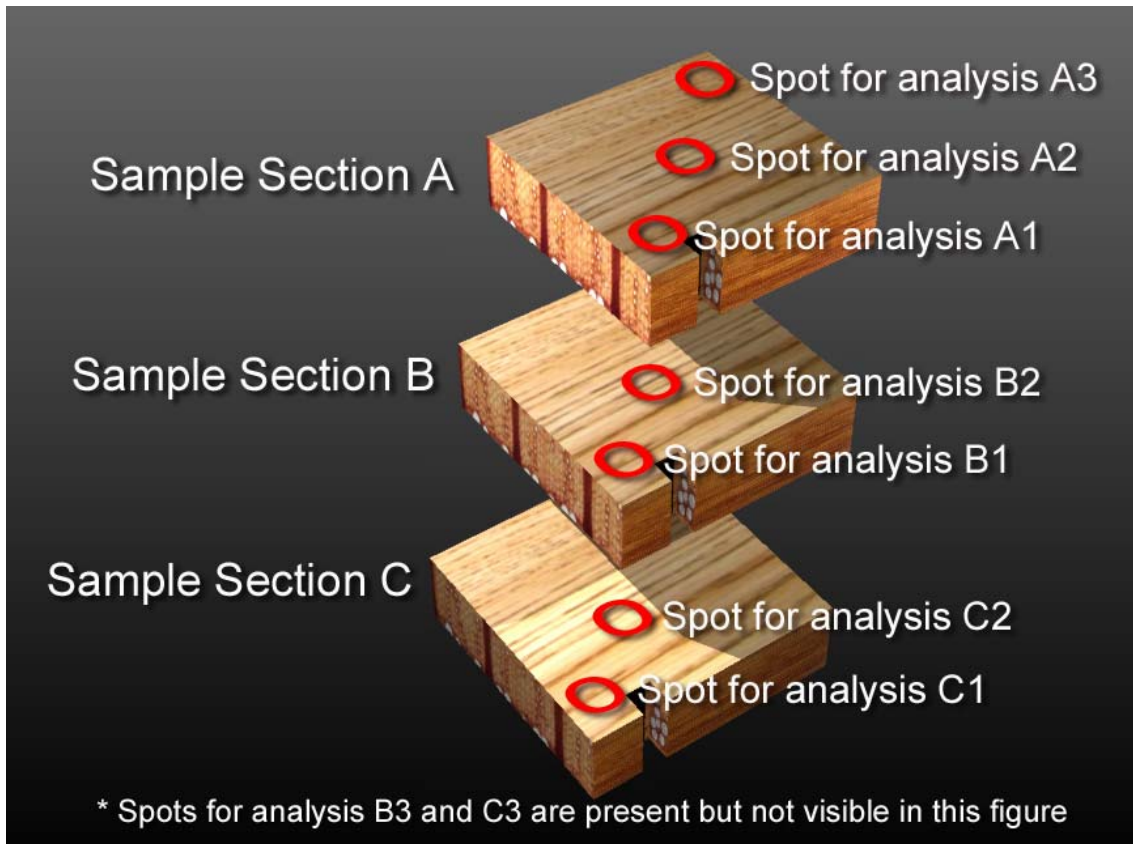


Figure 22. Spots for analysis. 3D reconstruction of the approximate position of the nine spots (three spots per section) selected for chemical analysis in every sample.

The different instruments employed for the chemical and microscopic analyses require that the sub-samples be absolutely dry. The waterlogged sub-sample (WS) and the EDMA sub-sample (ES) were waterlogged. Therefore, in order to conduct chemical analysis on these two samples they were dried with the assistance of a freeze dryer. A freeze dryer is able to remove the water from the wood samples, avoiding the collapse of the wood structure. In order to freeze-dry the samples, they have to be frozen prior to being dried in the freeze dryer. Therefore, the samples were first flash frozen. The samples were immersed into a cooling bath of dry ice and acetone for several minutes.



Dry ice and acetone cooling baths can provide temperatures down to about  $-78\text{ }^{\circ}\text{C}$ . After flash freezing the samples were dried in a freeze dryer for 12h at  $-55\text{ }^{\circ}\text{C}$  under a vacuum pressure of 4 millimeters of mercury (mmHg) (Figure 23).



Figure 23. Three images of the freeze drying process. Left and center, samples are flash frozen in acetone and dry ice; right, the CRL freeze dryer used to dry the samples.

## CHAPTER VI

### ANALYSIS OF THE SAMPLES

#### **Physical Documentation and Analysis**

All the samples and sub-samples were documented in detail by taking complete sets of photographs and macrophotographs of each wood plane in every sample. Photographs were taken before and after every step or phase of the experiment. As a result more than 300 photographs of the samples and sub-samples were taken throughout the experiment.

Several physical parameters and characteristics of the sub-samples were monitored and documented. During the experiment, throughout the re-conservation process, several physical values were monitored in order to detect variations. Color, linear dimensions, weight, volume, and specific gravity were measured before and after each of the three re-treatments.

#### ***Color of the Samples***

Accurate methods for obtaining a quantitative measurement of color in archaeological wood had been proposed (MacLeod and Gilroy 1987). This method offers accurate results but requires the use of an expensive digital colorimeter (i.e., Minolta® Chroma Meter). The colorimeter analyzes the color giving values in the CIE 1976 ( $L^*$ ,  $a^*$ ,  $b^*$ ) color space (CIELAB) system. This system assumes that color space is

Euclidean (i.e., three dimensional), and the colorimeter calculates the straight line distance between coordinates of the sample and the standard.

Another way to calculate quantitative changes using the CIELAB system can be achieved by using image software as Photoshop®. This image software offers the possibility of obtaining CIELAB values from a particular spot from a color-corrected photo of the sample. The CIELAB values will allow one to quantitatively measure variations in color, from one photograph to another, by following the method and equation proposed by MacLeod and Gilroy (1987). However, in order to obtain accurate results both, pre-conservation and post-conservation photographs should be taken with a color scale at the same light conditions, with the same camera and the same camera settings. Otherwise, the CIELAB values will differ due the different conditions and not necessarily due changes in the samples. However, if all parameters and light conditions are controlled and repeated, before and after conservation, reasonably accurate quantitative results can be achieved without the use of an expensive digital colorimeter.

For this experiment, however, the author employed visual observations with the aid of a Munsell® Soil Color Chart (Munsell 1946), which has along history of use in archaeology. The Munsell® system divides colors into groups that share distinctive characteristics.

*Hue* is the quality which distinguishes one color family from another, such as red from yellow or green from blue. There are five principal groups or *hues*: Red, Yellow, Green, Blue, and Purple, along with five intermediate hues

halfway between adjacent principal hues. Each of these ten steps is then broken into ten sub-steps, so that 100 hues are given integer values.

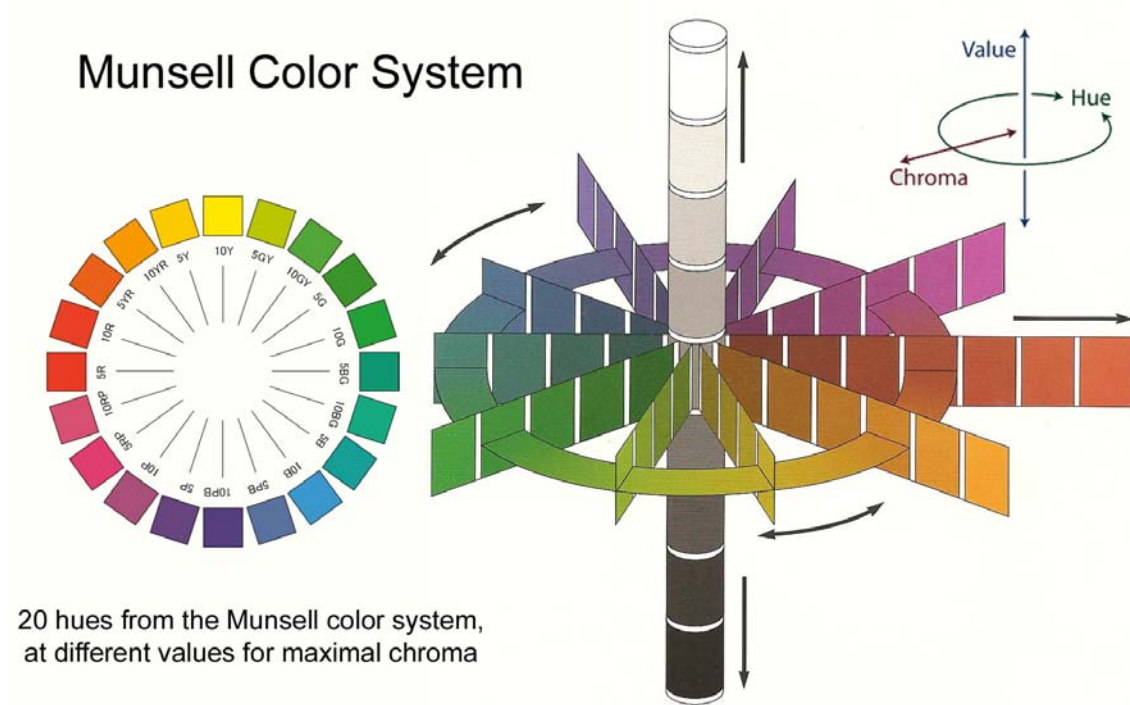


Figure 24. Munsell® Color System. Spatial distribution of color in the Munsell color system. (After Long and Turner Luke 2001).

*Value* is the lightness or darkness of any color. It varies vertically along the color solid, from black (value 0) at the bottom to white (value 10) at the top. Neutral grays lie along the vertical axis between black and white.

*Chroma* is the strength or weakness of a color. Measured radially from the center of each slice, it represents the intensity or saturation of a color. Vivid soil colors are in the range of approximately 8 (Munsell 1946:14-24).

A color is fully specified by listing the three numbers for hue, value, and chroma. For instance, the soil color chart most used for this research was the Munsell® Soil

Color Chart HUE 10YR. 10YR meaning the color yellow-red (YR) hue band. The complete specification of a particular color from this chart will include its value and chroma. Thus, HUE 10YR 5/8 stands for yellow-red, 5/ meaning medium lightness, and a chroma of /8, which in this particular case is the maximum saturation possible (Munsell 1946:25-30).

The color of the samples used in this experiment were compared and categorized accordingly to the Munsell® Soil Color Chart designations. All observations were made at indirect natural day light approximately at noon time. The observations, yet biased, offer qualitative results of the color in order to detect variations thorough the re-conservation process. By comparing the pre-conservation and post-conservation observations and their Munsell® values, the variations in value and chroma can be measured. Therefore, even though the observations are biased, some degree of quantitative data can be obtained by measuring the changes in value (i.e., lightness) and chroma (i.e., saturation) of the Munsell® Soil Color Chart. All the color data obtained from the sub-samples, before and after re-conservation, is compiled in the Appendix I of this thesis.

### *Linear Measurements and Weight*

Linear measurements were taken with the aid of a metric caliper. Of each sample and sub-samples three linear measurements were taken: longitudinal, radial and tangential axis (Figure 25).

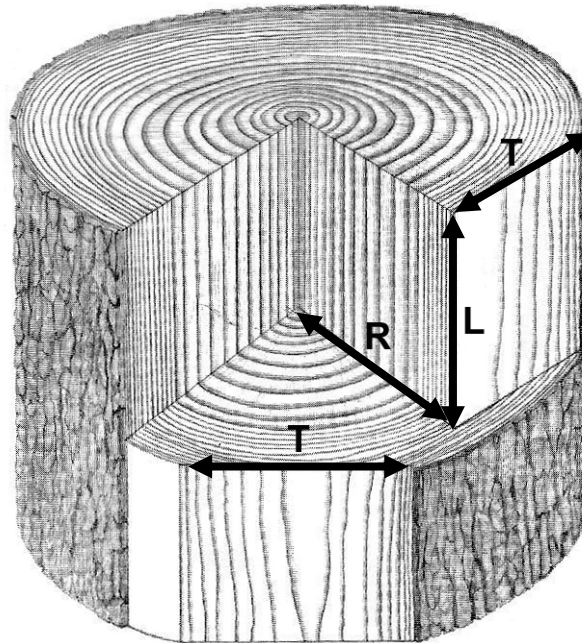


Figure 25. Spatial distribution of the three axes of wood. The three axis were measured on each sample: L, longitudinal; R, radial; T, tangential (After Hoadley 1990:12).

The weight of each sample and sub-samples was measured before and after each of the re-treatments by a precision digital scale in order to detect variations thorough the re-conservation process. All the measurements obtained from the sub-samples, before and after re-conservation, are compiled in the Appendix I of this thesis.

### *Volume: 3D Scanning*

The volume of each sample and sub-sample was recorded using 3D scanning technology. The original three wood samples were first scanned at the *Vasa* Museum by Arvid Engström. Structured-Light 3D optical scanner was used to collect the data with a Gom® ATOS optical digitizer. Optical digitizers, also known as structured-light 3D scanners, project a pattern of light on the subject and look at the deformation of the pattern on the subject. The pattern is projected onto the subject using an LCD projector. A camera, offset slightly from the pattern projector, looks at the shape of the pattern and uses a technique similar to triangulation to calculate the distance of every point on the pattern (Figure 26).

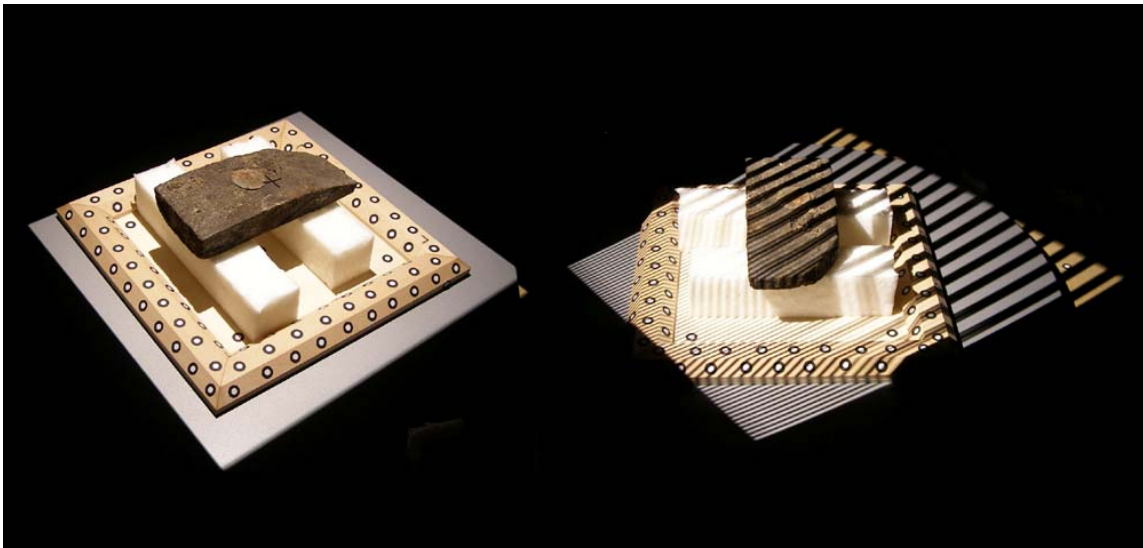


Figure 26. Two images of the optical scanning process. Left, PEG sample placed on the scanning template; right, projected pattern onto the sample using an LCD projector.

The data recorded by the camera is then interpreted by a computer program, which creates a virtual replica of the artifact. The software used was Atos® v6 which models a 3D mesh of the sample (Figure 27).

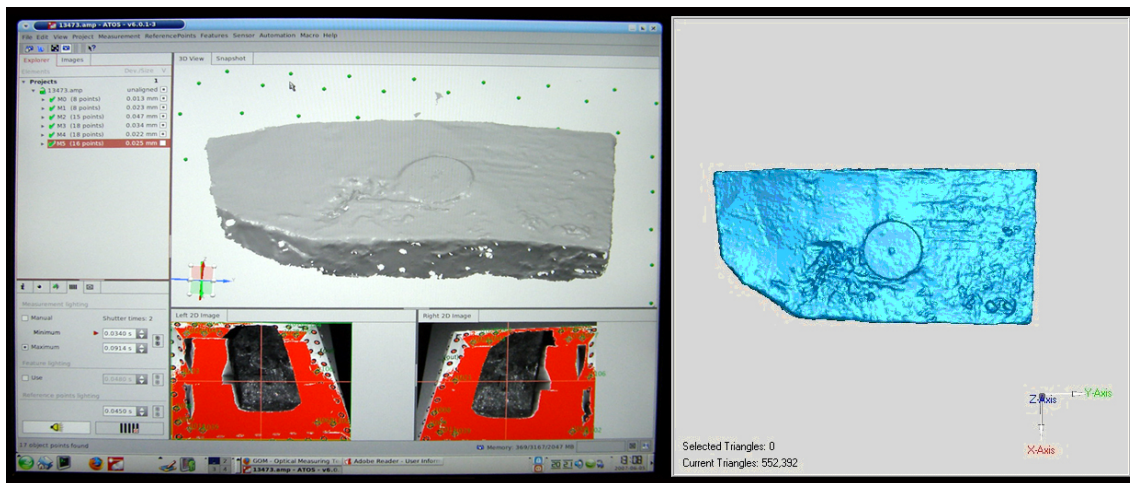


Figure 27. Two images of the interface of the scanning process: left, program Atos® v6 interface; right: final 3D mesh of the PEG sample.

Upon arrival to TAMU, the three original samples were scanned again at the Wilder Imaging Laboratory. The samples were scanned with a Minolta® Vivid 910 3D laser digitizer by Blanca Rodriguez and the author. A 3D laser digitizer is an active scanner that uses laser light to probe the subject. The scanner finds the distance of a surface by timing the round-trip time of a pulse of light. A laser is used to emit a pulse of light, and the amount of time before the reflected light is seen by a detector is timed.



Scanning the samples for a second time was conducted for comparing the two types of 3D scanning technologies employed. Despite the different types of scanners and technologies used, first used at the *Vasa* Museum and later at TAMU, the 3D results of the scans were identical. Then the plan was to continue scanning the sub-samples resulting from the division of the three main samples. Therefore, after the original samples were cut, the resulting sub-samples were scanned in order to obtain their respective volumes (Figure 28). Once the re-conservation procedures were completed, the sub-samples selected for re-conservation were scanned again in order to detect variations in volume through the re-conservation process.

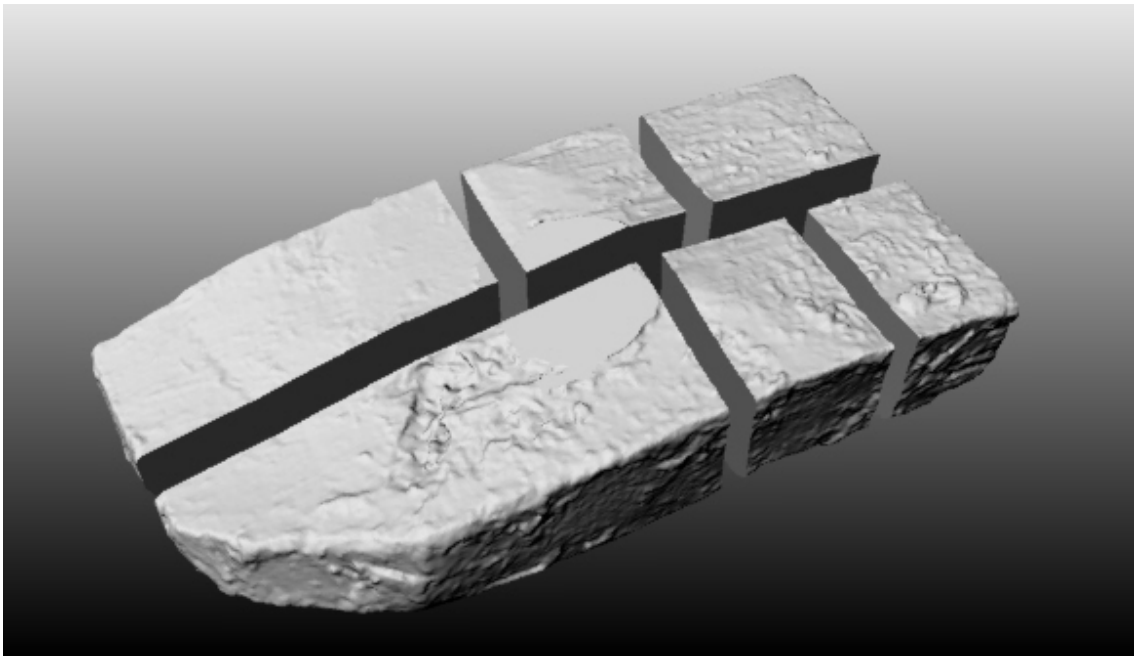


Figure 28. 3D digitalization of the six sub-samples obtained from the PEG sample.

The numerical volume values of the samples and sub-samples were obtained with the aid of Rhinoceros® 3D modeling software (Figure 29). Besides the volume values of the sample, Rhinoceros® also provides precise linear measurements of the scanned samples, which were used to compare and improve the linear measurements taken with a caliper. All the volumes obtained from the sub-samples, before and after re-conservation, are compiled in the Appendix I of this thesis.

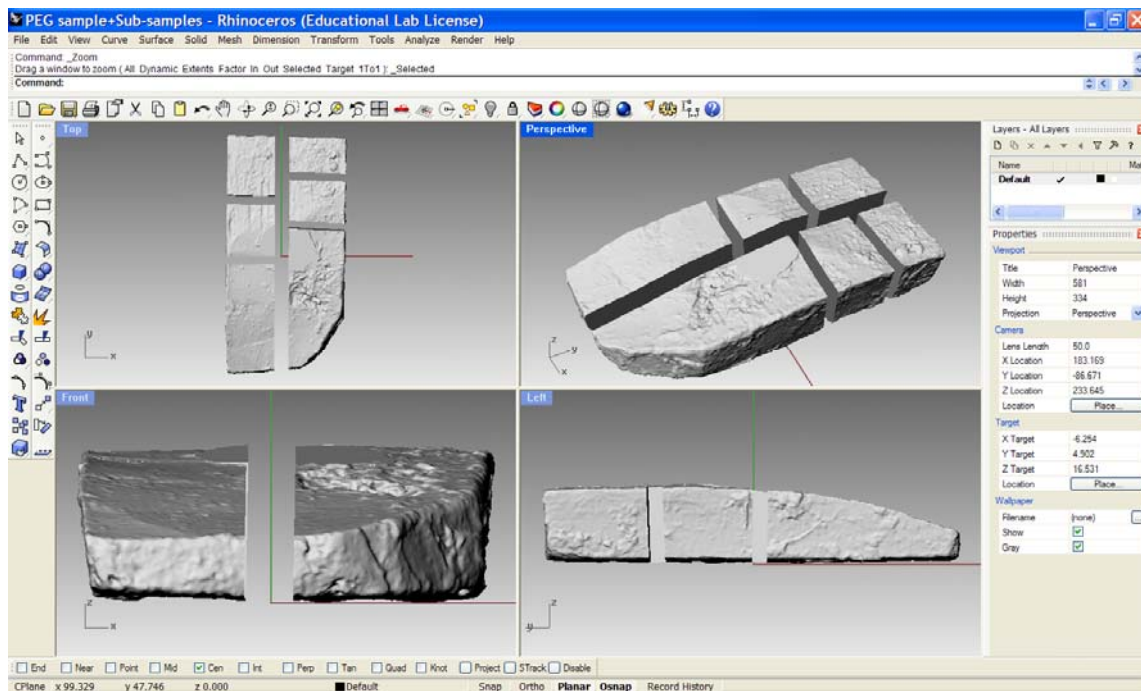


Figure 29. 3D modeling software Rhinoceros® interface showing PEG sub-samples.

### ***Specific Gravity***

Specific gravity is relative density, calculated as the ratio of the density of a substance (in this case wood) to the density of water (i.e., 1 g/cm<sup>3</sup>). To avoid the effect of the weight of water in the wood, oven-dry weight (i.e., 0% of moisture) is used for standard measurements of specific gravity (Hoadley 1990:47). The specific gravity of each sub-sample was calculated with its weight and volume in order to detect variations thorough the re-conservation process. In this experiment, all the specific gravities of the sub-samples were calculated indoor at room temperature weight. Therefore, an approximate 8% of moisture can be expected at these conditions (Hoadley 1990:49). This 8% differs from the 0% of moisture content used for the standard measurement. Thus, an optimal final specific gravity value should be slightly greater than the standard. All the specific gravities obtained from the sub-samples, before and after re-conservation, are compiled in the Appendix I of this thesis.

### **Wood Analysis**

#### ***Lumber Board Reconstruction***

Because of the arrangement of growth in the tree, as well the orientation of the cells, the structure of the wood is described in three-dimensional terms. One plane is perpendicular to the stem axis and is termed cross-sectional plane or transverse plane, typically observed at the end of a log (Figure 30). Because the tree cross-section is analogous to a circle, a plane passing through the pith of the wood (as a radius of the circle) is called radial plane. A plane parallel to the pith but not passing through it forms

a tangent to the circular growth-ring structure and is termed tangential plane (Hoadley 1980:7).

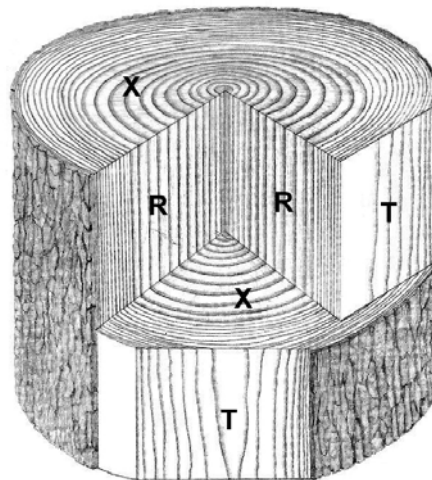


Figure 30. The three planes of wood: X, cross-sectional; R, radial; T, tangential (After Hoadley 1990:12).

There are different ways or methods of sawing lumber logs to produce boards (Figure 31). Two of the most popular ways are gang saw, which produces flat-grained or flatsawn boards; and quarter saw, which produces edge-grained or quartersawn boards (Hoadley 1980:207-209).

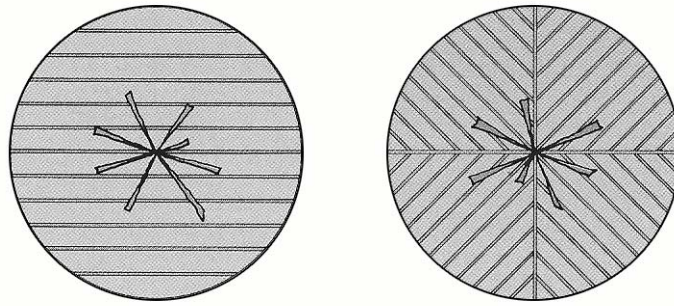


Figure 31. Two different techniques of sawing lumber. Left, gang saw method, which produces flatsawn boards; right, quarter saw method, which produces quartersawn boards (After Hoadley 1980:209).

The way or method in which any piece of wood was originally sawn from the lumber could be reconstructed by measuring circular growth-ring structure of the cross-sectional plane. Although the curvature of the growth ring is not geometrically regular, by reconstructing this circumference of the growth ring some information can be gathered.

In this research, the reconstruction of the circumference was achieved by using the tools of the 3D modeling software Rhinoceros®. This program allows creating circles from three points of reference. Thus, over a macrophotography of the cross-sectional plane of the samples, three points were placed over the same growth ring; two at the extremes of the growth ring and one at the center. Rhinoceros® software is then able to reconstruct the complete circle of the growth ring as shown in Figure 32.

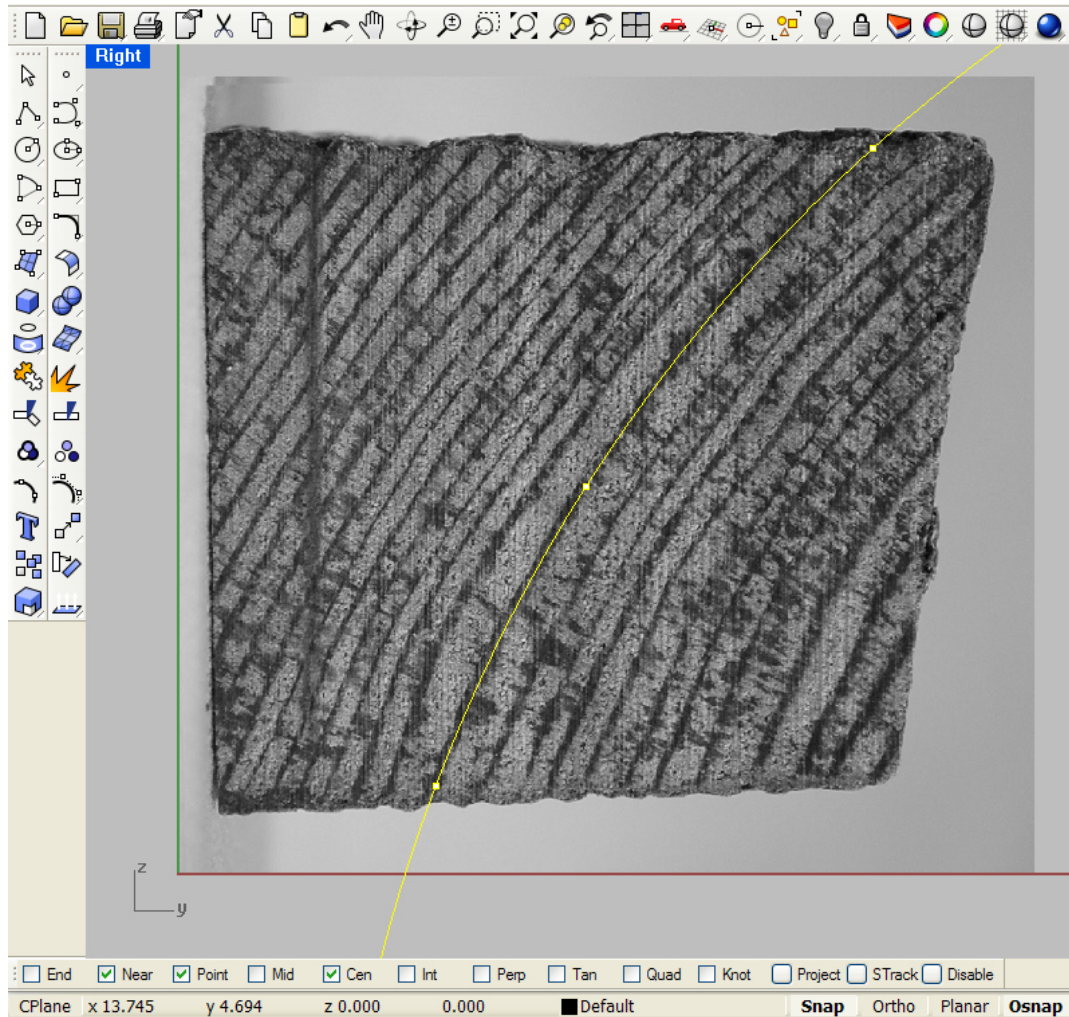


Figure 32. Image from the Rhinoceros® software interface. This software was used to reconstruct the complete circumference of the growth ring from the PEG sample. Three points selected on the same ring and the circle resulting from their position (yellow arch).

By reconstructing the complete circle of the growth ring, four factors can be reconstructed: the exact position of the board related to the log, the type of sawing method followed to saw this board, a minimum thickness of the log, and a minimum age of the log at the time when it was processed. This last factor could be achieved by

establishing the relation in between the average number of growth rings by linear centimeter and the estimated total thickness of the log (Hoadley 1980:1).

Following the explained procedure, it is possible to establish that the original oak board, from which the waterlogged sample comes, was the result of flat-grained or flatsawn boards (Figure 33). In these types of boards, the growth of the rings is approximately parallel to the wide faces or tangential plane. The growth rings form angles of anywhere from  $45^{\circ}$  to  $90^{\circ}$  with the surface (Hoadley 1980:8; 207-209). The log itself had a minimum thickness (i.e., diameter) of *circa* 28 cm at the time it was sawn to produce boards.

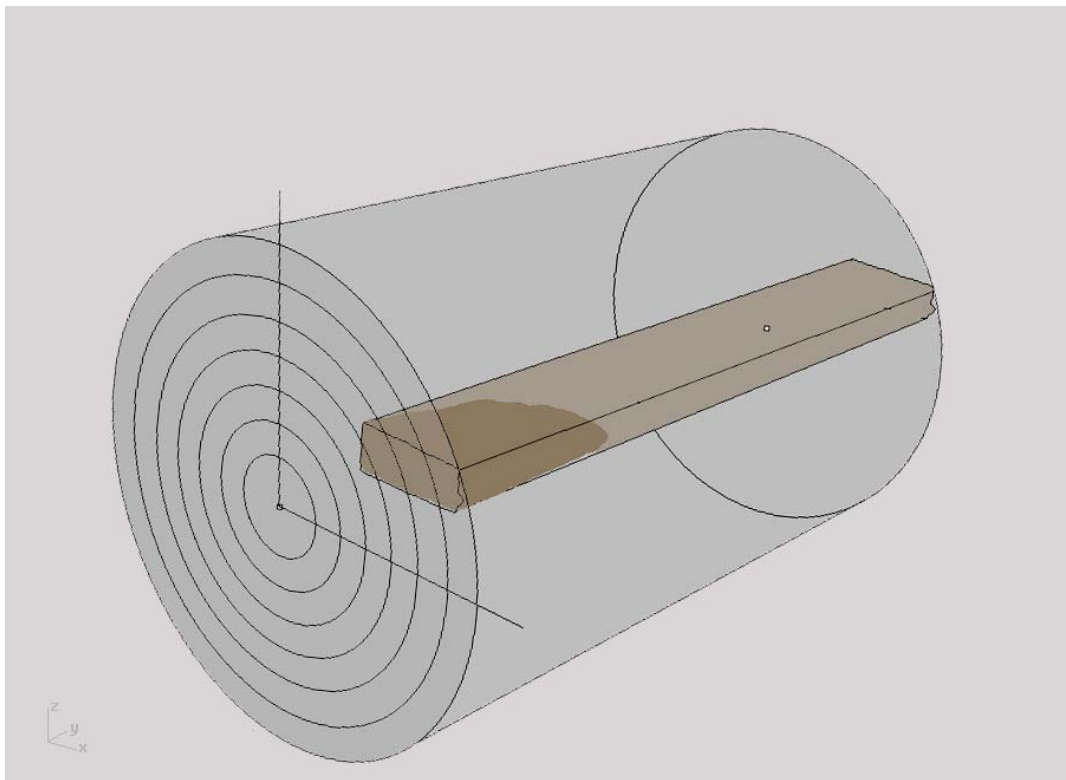


Figure 33. Reconstructed position of waterlogged sample. Reconstructed position within the log of waterlogged sample (dark), the flat-grained or flatsawn board (shaded) from which it came, and the minimum log thickness.

The original pine board, from which the EDMA sample comes, was the result of a log sawn to produce flat-grained or flatsawn boards (Figure 34). In these types of boards, the growth of the rings is approximately parallel to the wide faces or tangential plane (Hoadley 1980:8; 207-209). The log itself had a minimum thickness (i.e., diameter) of *circa* 32 cm at the time it was sawn to produce boards.

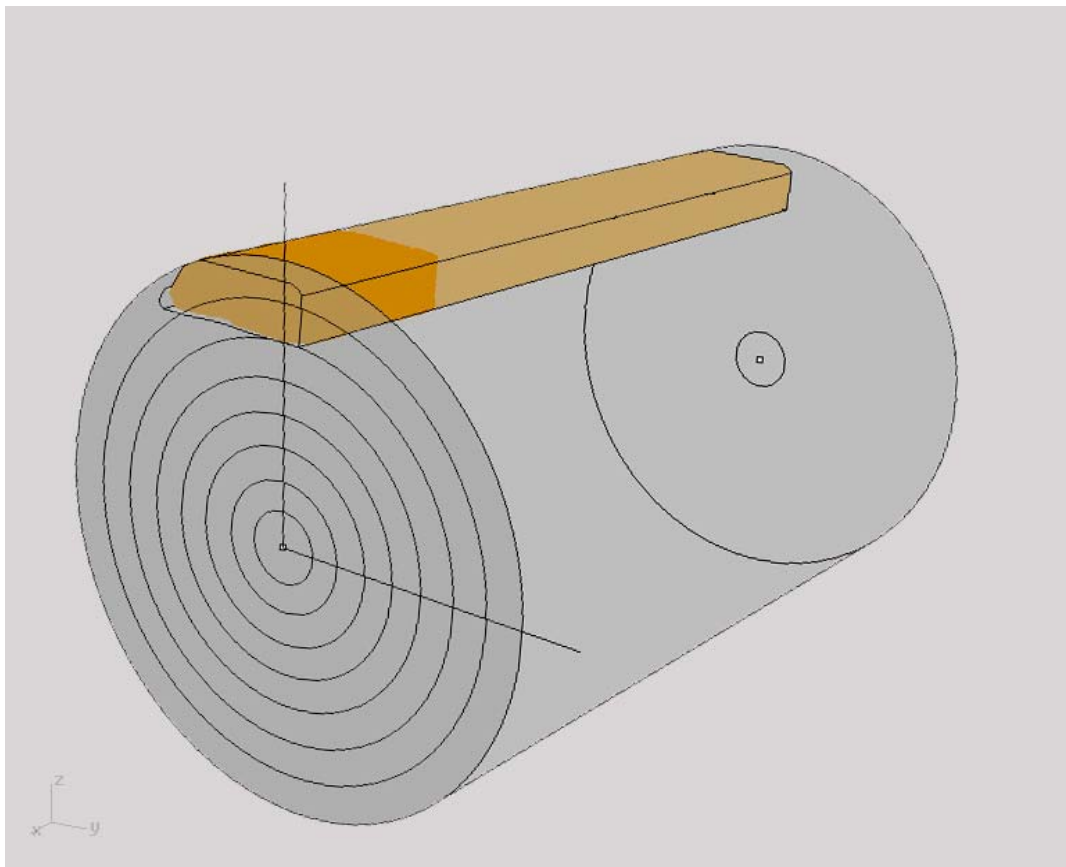


Figure 34. Reconstructed position of EDMA sample. Reconstructed position of EDMA sample (dark) within the log; the flat-grained or flatsawn board (shaded) from which it came from, and the minimum log thickness of the log are shown.



The original pine board, from which the PEG sample comes, was the result of flat-grained or flatsawn boards (Figure 24). In these types of boards, the growth of the rings is approximately parallel to the wide faces or tangential plane (Hoadley 1980:8; 207-209). The log itself had a minimum thickness (i.e., diameter) of *circa* 29 cm at the time it was sawn to produce boards.

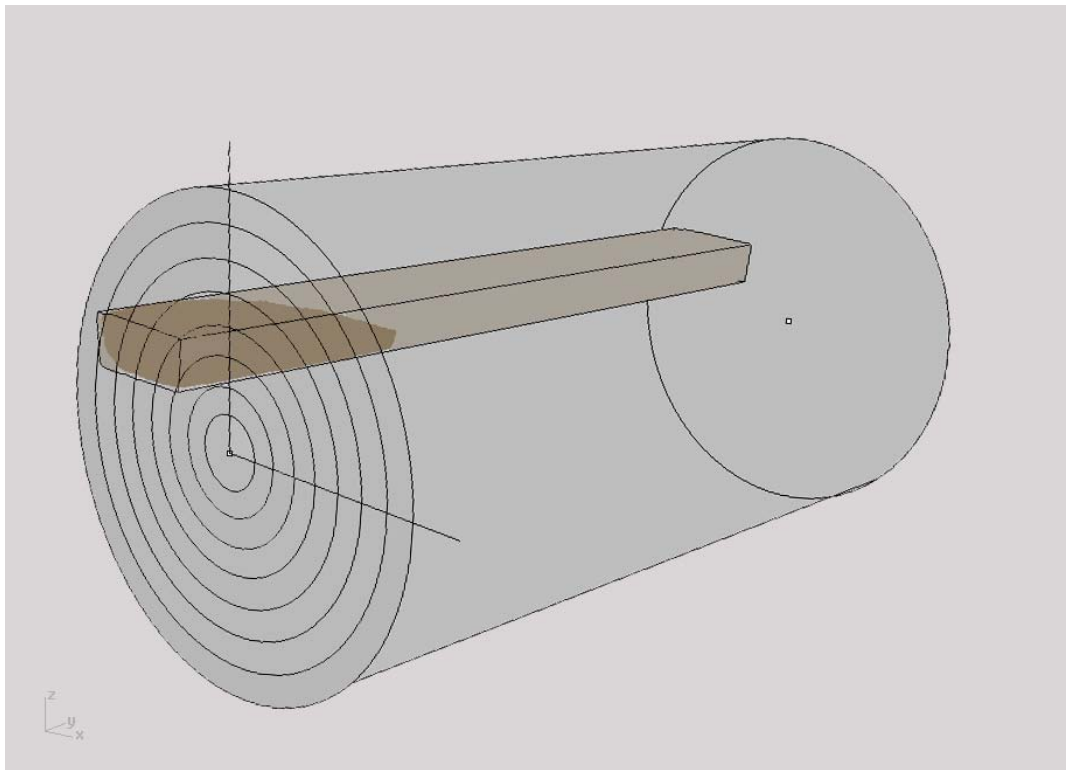


Figure 35. Reconstructed position PEG sample. Reconstructed position of PEG sample (dark) within the log; the flat-grained or flatsawn board (shaded) from which it came from, and the minimum log thickness of the log are shown.

### ***Water Percentage***

Brorson-Christensen (1970) followed by de Jong (1977:295), devised a classification scheme to group wood according to the percentage of sound wood versus degraded in three different classes: Class I > 400% of water; class II 185-400% of water; and class III < 185% of water (Grattan 1987:67). In this method, which currently is still used as standard, the amount of water contained in the wood, or moisture content, is calculated following this formula (Grattan 1987:67; Hamilton 1996:26):

$$\% \text{ H}_2\text{O} = \frac{\text{Weight of the waterlogged wood} - \text{Weight of the oven dried wood}}{\text{Weight of the oven dried wood}} \times 100$$

The formula was applied in order to identify which type of waterlogged wood represented each of the samples. Thus, the amount of water of each sample was calculated by weighing a sub-sample saturated with water and measuring the same sub-sample after complete dehydration in a ventilated oven, for 24 hours at 100 °C (Hoadley 1990:49). The results determined that the waterlogged sample (WS) and the PEG sample (PS) contained a percentage 92% and 21% respectively, which is considerably smaller than 185%, Class III of waterlogged wood (Grattan 1987:67). In the case of the EDMA sample (ES), the results determined that the percentage of water contained was 301%. Above 185% and below 400% of moisture content, this corresponds to a Class II of waterlogged wood (Grattan 1987:67). These ratios of water content are similar to the results obtained on previous studies conducted on *Vasa* wood (Håfors 1993:57).

## Wood Identification

Microscopic analyses of the samples were conducted in order to identify the wood species of the samples. Thin slides were taken from the transverse surface of each of the three wood samples by hand cut following the procedure described by Hoadley (1990:78-89). An optical microscope with a digital camera was used to obtain photos of the thin sections from the samples.

The identification of the samples determined that the waterlogged sample (WS) at the genus level is oak (i.e., *Quercus*). This identification contradicted the author's assumption that the sample was pine (i.e., *Pinus*) as it was presumed to be when it was selected at the *Vasa* Museum in June 2007. The exact species of the northern European oak cannot be identified below the genus level based on the characteristics of the wood (Hather 2000:48). The oak could be either *Quercus robur* sp. or *Quercus patraea* sp., which both taxa have a native distribution in Sweden (Hather 2000:48). Other studies conducted on *Vasa* wood (Fors 2005:9; Björdal and Nilsson 2007:486; Iversen et al. 2007:494) identified the oak from the *Vasa* as *Quercus robur* sp.

The EDMA sample (ES) and the PEG sample (PS) were both identified at the genus level as pine (i.e., *Pinus*) and at the species level as *Pinus sylvestris* sp., as expected (Hather 2000:48; Fors 2005:9; Björdal and Nilsson 2007:486). The identification of the wood species was conducted with the assistance of Dr. Raquel Carreras Rivery, Professor at Instituto Superior de Arte (ISA), La Habana, Cuba.

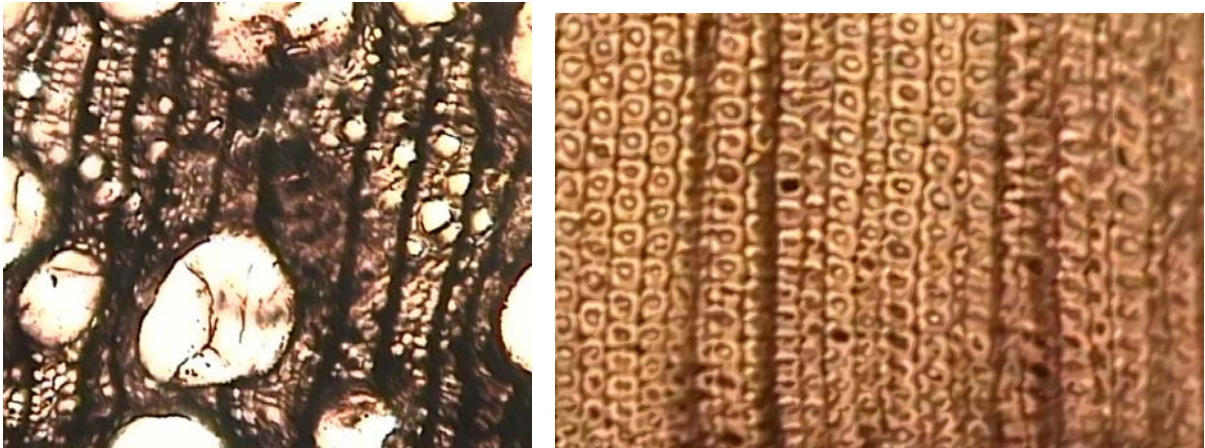


Figure 36. Two microscopic photographs of wood slices. Left, waterlogged sample (WS) identified as *Quercus robur sp.*; right, EDMA sample identified as *Pinus sylvestris sp.* (both images 100x magnification).

### **Microscopic Analysis**

Environmental Scanning Electron Microscopy (ESEM) is a scanning electron microscope (SEM) that allows a gaseous environment in the specimen chamber, allowing the samples to be moist. On the other hand, all other electron microscopes operate under high vacuum and require that the samples are completely dry. ESEM was conducted as an effective analytical tool to visualize, document, and compare, at the microscopic level, the reagents used in the re-conservation of the wood samples. Before and after any re-conservation treatment, ESEM analyses were conducted on an Electroscan ESEM-E3 from Microscopy and Imaging Center (MIC) at TAMU. The Electroscan ESEM-E3 acquisition was supported by a National Science Foundation Grant No. EC59214314. This environmental SEM is capable of operating at pressures as high as 50 torr down to pressures comparable to most SEMs. It allows flexibility in

specimen types, often with minimum sample preparation, for viewing in their "natural" states. The ESEM operates in a magnification range of 100 x to 100,000 x, and has guaranteed resolution of 5.0nm. The ESEM analyses and documentation of the samples were made by Catherine Sincich and the author with the assistance of Rick Littleton at Microscopy and Imaging Center (MIC) TAMU. Some of the micrographs obtained with the ESEM analyses are presented on Chapter VII.

### **Elemental Analysis**

As explained above, after being cut into sub-samples and before re-conservation, the three different wood samples were analyzed in order to identify and quantify the presence of foreign elements. Three were the elements in which the analyses focused to identify: iron compounds, sulfur, and PEG. For the identification and quantification of iron compounds and sulfur, two different analysis were conducted with two different systems: Electron Dispersion Spectroscopy -EDS-, and X-ray Photoelectron Spectrometry -XPS-. For the identification and quantification of PEG, one analysis was conducted: Fourier Transform Infrared Spectroscopy -FTIR-.

### *EDS Elemental Analysis*

EDS analysis is an analytical technique used for the elemental analysis or chemical characterization of a sample. EDS analysis was conducted for the identification and quantification of iron compounds and sulfur present into the wood samples. The analyses were performed on a JEOL JSM-6400 scanning electron microscope equipped with secondary, backscatter, and energy dispersive spectroscopy detectors, and it uses a tungsten filament source. The JSM-6400 is equipped with a PGT EDS System. This software-oriented, analytical-grade SEM is capable of acquiring and digitizing images (Figure 37). Acceleration voltages from 0.2 to 40kV, a magnification range of 10 to 300,000 x, and a guaranteed resolution of 3.5 nm allow an operator to achieve excellent results. The EDS analysis provides a micrograph of the surface analyzed with EDS spectrum of the elements identified. The analyses of the samples were made by Dr. Michael Pendelton at Microscopy and Imaging Center (MIC) at TAMU.

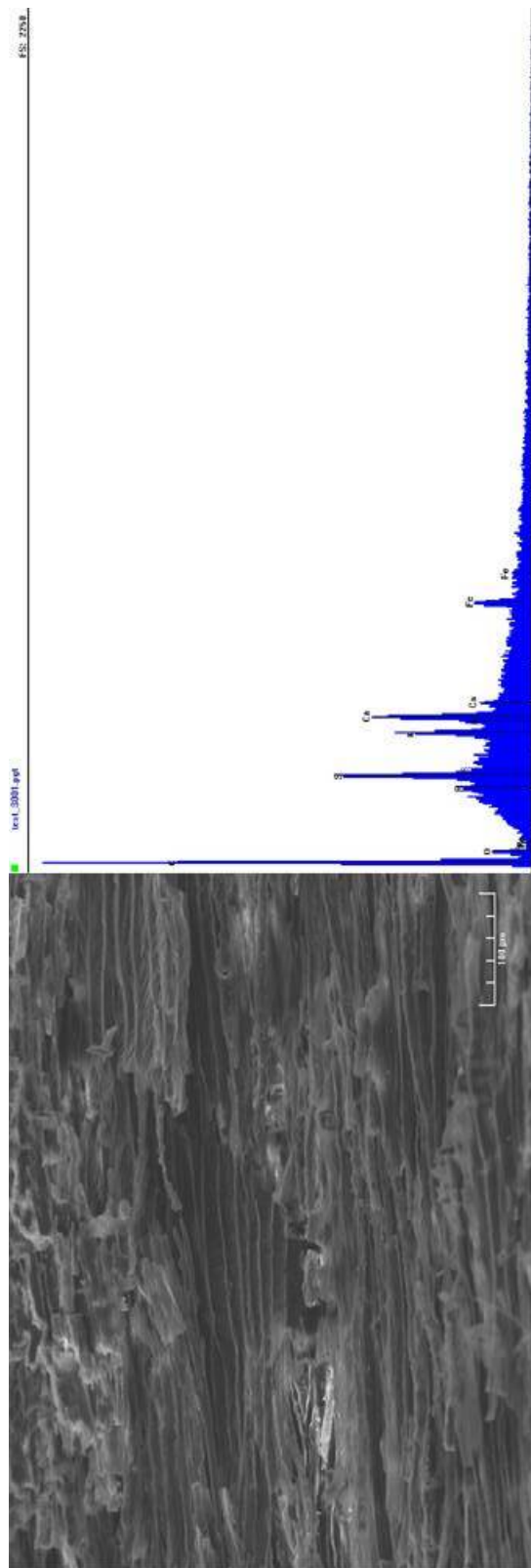


Figure 37. Two images from the EDS analysis of WS1-A2 spot. Left, electron micrograph; right, EDS spectrum of the main elements identified (i.e. C, O, Fe, S and Ca).

### *XPS Elemental Analysis*

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state, and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 nm to 10 nm of the material being analyzed. A Kratos Axis Ultra Imaging X-ray photoelectron spectrometer (XPS or ESCA for electron spectroscopy for chemical analysis) was used for the identification and quantification of iron compounds and sulfur (Figure 38). The XPS analyses of the samples were conducted by Dr. Gang Lian at the Materials Characterization Facility at TAMU.



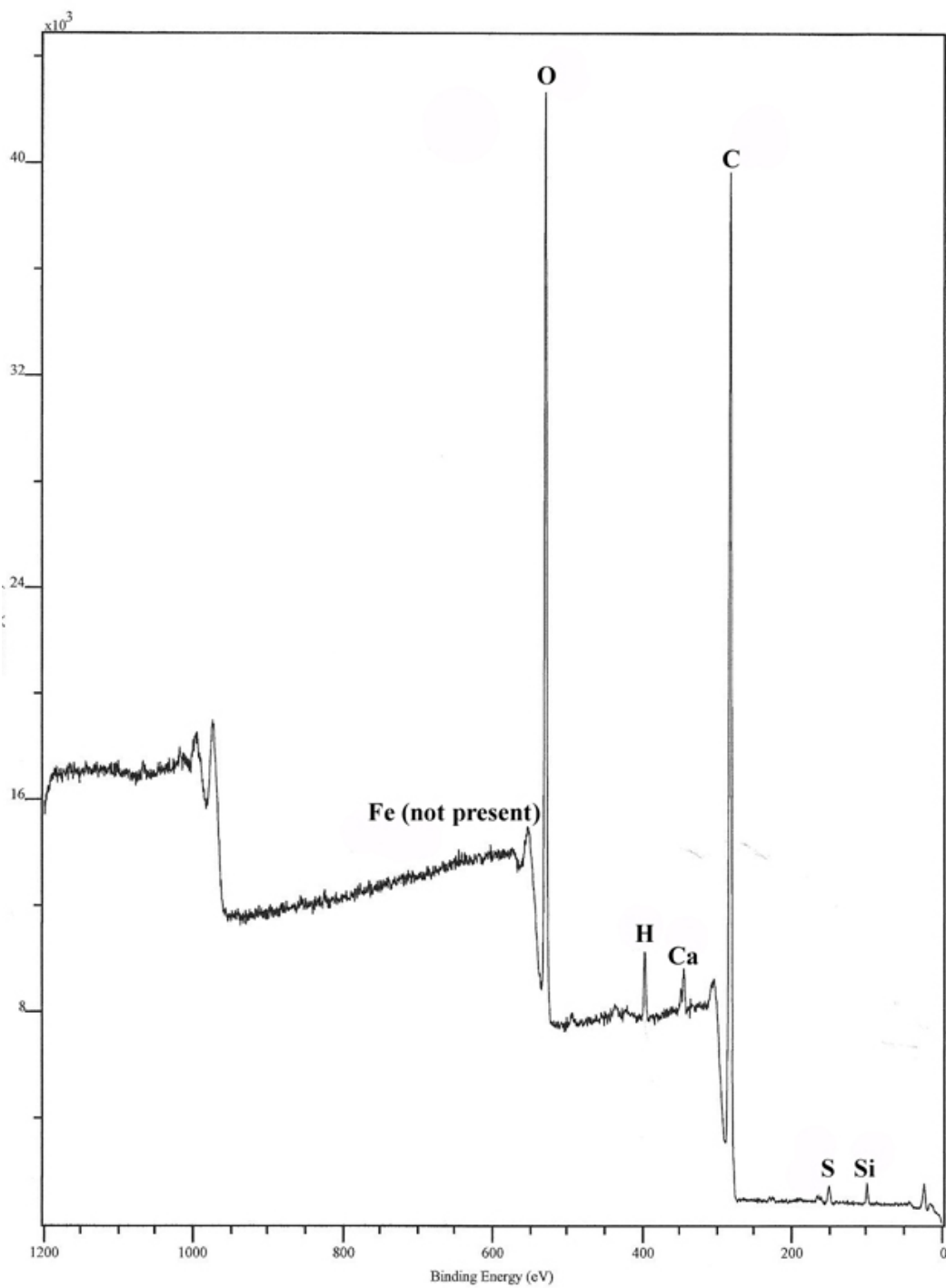


Figure 38. Example of XPS spectrum. Elements identified in sample ES1-A1 (i.e. C, O, Fe, S, Ca and Si).

### ***Elemental Analysis Results***

The results obtained by the EDS analysis were compared with the ones obtained by XPS analysis. A total of 27 spots (9 per type of sample) were analyzed by EDS analysis and by XPS analysis. Therefore, a total of 56 spots, plus some extra special spots, were analyzed. In this chapter the average result of each wood sample will be presented.

#### Elemental Analysis Results of WS

In the waterlogged sample, the average presence of iron in the analyzed spots was minimal, and practically no peak appeared on the spectrum of the analysis; in general the average atomic concentration of iron was below 0.2%. Therefore, the presence of iron compounds in the waterlogged sample could be considered minimal or not present. These ratios are similar to those acquired by previous studies conducted on wood samples from the *Vasa* (Håfors 2001:123).

The presence of iron compounds in timbers from shipwrecks has been studied (MacLeod and Richards 1996), and it is the result of the oxidation of structural iron elements (i.e., bolts, fittings, etc.) and objects (i.e., cannons, ammunition, etc.) present on the ship at the time of its wreckage (Hocker et al. 2007:470). However, the lack of iron compounds on the waterlogged sample demonstrates that even though it is likely to find iron compounds in timbers from shipwrecks, this not always happened to all the artifacts within the shipwreck. Therefore, case-by-case analysis would be desirable, and generalizations should be avoided as the situation permits.

The presence of sulfur in the analyzed spots differs between that found in the internal spots and the external spots. The presence of sulfur in the internal surface of the sample is slightly smaller than that on the external surface. In the external spots the sulfur was present in small quantities (i.e., small peak in the spectrum of the analysis), reaching an average of 0.25% of atomic concentration. Therefore, the presence of sulfur in the external surfaces of the sample could be interpreted as slightly present. The occurrence of sulphide salts in ships' timbers is well documented (Jespersen: 1987; MacLeod and Kenna 1990), and it is not surprising that they would be found in the wood samples from the *Vasa* (Sandström et al. 2001:55).

#### Elemental Analysis Results of ES

In the EDMA sample, the presence of iron at the analyzed spots was nonexistent (i.e., no peak appeared on the spectrum of the analysis). Therefore, the presence of iron compounds in the EDMA sample could be considered as not present. These analyses demonstrate that the extraction of iron compounds conducted at the *Vasa* conservation laboratory (Almkvist et al. 2004) was highly successful.

The average presence of sulfur in the analyzed spots varies between the internal spots and the external spots. In the external spots the presence of sulfur reached an average of 0.25% of atomic concentration (i.e., a small peak in the spectrum of the analysis). Therefore, the presence of sulfur in the external surfaces of the sample could be interpreted as slightly present.

### Elemental Analysis Results of PS

In the PEG sample, the presence of iron was not homogeneous. In some of the analyzed spots the presence of iron was minimal (i.e., practically no peak appeared on the spectrum of the analysis). Whereas in other spots, iron was detected on an average ranged from 0.45% to 1.2% of atomic concentration. Therefore, the presence of iron compounds in the PEG sample could be considered as not homogeneous. Also, in those places where its presence was detected it could be interpreted as slightly present. These ratios are similar to those acquired by previous studies conducted on wood samples from the *Vasa* (Håfors 2001:123).

The average presence of sulfur in the analyzed spots varies slightly between the internal spots and the external analyzed spots. The presence of sulfur in the internal spots is slightly smaller than those in the external surface. In the external spots the presence of sulfur reached an average of 0.55% of atomic concentration (i.e., represented by a small peak in the spectrum of the analysis). Therefore, the presence of sulfur in the external surfaces of the sample could be interpreted as slightly present.

It should be mentioned that other foreign elements were found during the analysis. In general, on all the spots analyzed showed small quantities of calcium, and silicon were detected by both analytical methods applied. The calcium corresponds to that of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), a common mineral deposited in lake and sea water; the silicon came from silicates commonly occurring from surface contamination (Sandström et al. 2001:78).

### **Compounds Analysis: Raman/FTIR**

Identification and quantification of PEG, silicone oil, and MTMS before and after each treatment was conducted by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Infrared spectroscopy (IR spectroscopy) is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. It can be used to identify compounds and investigate sample composition. Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range.

An integrated Raman/FTIR /AFM/NSOM system with nanoscale spatial resolution for materials research was used for the analysis in this experiment. The LabRam IR manufactured by Horiba Jobin Yvon provides highly specific spectral fingerprints that enable precise chemical and molecular characterization and identification. It offers the advantage of same spot analysis where the same position on the sample can be analyzed via both techniques without the need for any sample positioning or instrument adjustment. The Raman/FTIR analyses provide a spectrum of the substances identified (Figure 39). The Raman/FTIR analyses of the samples were conducted by Dr. Amanda Young at the Materials Characterization Facility (MCF) at TAMU. The Raman/FTIR/AFM/NSOM acquisition was supported by the National Science Foundation under Grant No. BES-0421409.

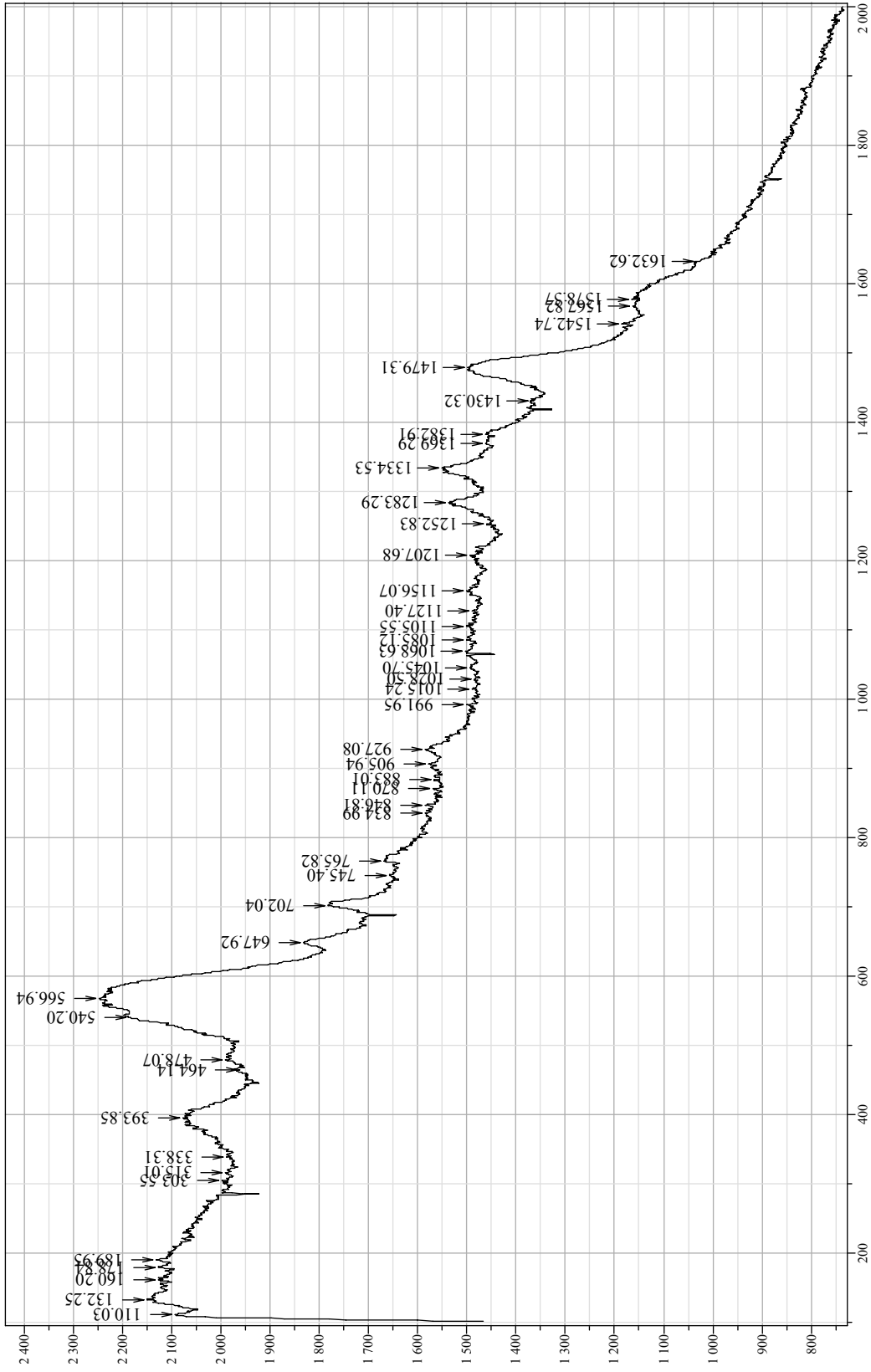


Figure 39. Example of Raman/FTIR raw spectrum of WS sample after conservation.

A total of 18 samples were analyzed by Raman/FTIR analysis. Samples for analysis were taken from the three main wood samples before the re-conservation procedures. Of each wood sample, two samples for analysis were taken: one analysis sample from the internal structure and another analysis sample from the external surface. Thus, six samples for analysis were taken before the re-conservation process. After re-conservation, two samples for analysis (i.e., internal and external) were taken from each of the six final re-treated wood samples. Thus, twelve samples for analysis were taken after the re-conservation treatment.

Raman/FTIR analysis is able to provide highly specific qualitative and quantitative results of any substances analyzed. The analyses were able to positively identify the specific spectrum or fingerprint each of the substances used to conserve the wood samples (i.e., PEG, silicone oil, and MTMS). However, the analysis presented some inconveniences derived from several factors.

One problem dealing with waterlogged wood is that water-soluble substances, such as starch and sugar, are the first to be leached from waterlogged wood along with other bonding materials. With time, through hydrolysis, cellulose in the cell walls disintegrates, leaving only a lignin network to support the wood. Over a long period of time, even the lignin will break down (Hamilton 1996:26).

Hence, when Raman/FTIR analysis are conducted on waterlogged wood samples, the results are compared with the lignin present in the wood, since it is the most lasting component of it and is much more likely to be present. Unfortunately, in some samples analyzed on this study the lignin of the wood was not detected, and therefore it was

difficult to establish a baseline to compare the rest of the substances. These difficulties to obtain results from the lignin could be the result of several factors. In any waterlogged archaeological wood, it is expected to have some degree of degradation of the wood and, therefore, some loss of lignin.

Some other problems arose while conducting the Raman/FTIR analysis for this study. The instrument used by Dr. Young at the Materials Characterization Facility is equipped with a 785 nm diode laser, which is not the most suitable for analyzing waterlogged wood. When some compounds, either in the wood or the preservatives used for conserving the wood, were irradiated with this wavelength they fluoresce and, as a result, a nonlinear background was obtained in all the spectra. If there was no fluorescence, the background of the spectra would be a flat line.

Also, keep in mind that the size of the analyzed samples was not very large (i.e., about 3 mm<sup>2</sup>). As a consequence, the exact mass present on the samples of each of the elements (i.e., wood, PEG, silicone oil, MTMS) was unknown, and therefore sum up the difficulties in establishing baselines for these different elements.

Moreover, the considerable amount of relative humidity in Texas and the complexity of all the different organic material present on each of the samples seemed be unforeseen issues during the process of acquiring data. As a result, the spectra obtained from the samples of this study have, in general, a considerable amount of noise.

Finally, from each type of treatment only two samples were analyzed (i.e., internal and external surfaces). Therefore, from the statistical point of view the scope of our study was limited, and hence the results have to be considered in relative terms and



from a conservative point of view. After all, Raman/FTIR analysis is a very good noninvasive spectrographic analytical technique but does not perform miracles.

For all of the above, the results obtained from the analyses were qualitative (i.e., they detect the presence or absence of the substances) but quantitative to some extent. Based on the results, it was possible to quantify if a specific substance, in a particular sample, was more or less abundant compared with another sample. Thus, it was possible to indicate if a certain treatment is able to remove certain substance. Also, it is possible to indicate if a specific substance is more or less present in one sample compared to another sample treated with the same substance. Unfortunately, due the sum of the problematic factors, the results were unable to provide specific percentages of the substances present or the specific percent difference that occurred from one sample to another. Hence Raman/FTIR analysis results from this study have to be taken in relative/rational terms rather than in absolute terms. The average results Raman/FTIR analysis will be presented in this chapter.

### ***Pre-Conservation Compound Analysis Results***

As expected, the pre-conservation Raman/FTIR analyses of the PEG sample indicated that PEG was present into the sample in large quantities. On the other hand, the pre-conservation Raman/FTIR analysis of the EDMA sample indicated that PEG is still present, although in small quantities. This finding is remarkable since the EDMA wood sample was submerged in aqueous solution for five years: first during the extraction of iron compounds with EDMA, from September 2002 to June 2005

(Almkvist *et al.*: 2005), and after the EDMA treatment from June 2005 to June 2007 immersed in tap water. The results of the analysis completely support previous studies that show that despite the type of consolidant used and its theoretical reversibility, no treatment is reversible at the molecular level (Horie 1982:3.2). Therefore, although PEG is a substance that theoretically can be removed from an artifact (i.e., reversible), it is not possible to completely eliminate it from the artifact, and this presence does limit how the artifact can be re-treated.

### ***Post-Conservation Compound Analysis Results***

As explained earlier, the post-conservation Raman/FTIR analyses undergo unexpected difficulties. As a result the analyses were able to detect the presence or absence of the substances, hence providing qualitative data. However, they were unable to quantify the exact amount of these substances present on each sample. Therefore the results were quantitative to some extent.

Even though the results were not quantitative in absolute terms, the general amounts of reagent (i.e., PEG, silicone oil, and MTMS) present in a sample coincided with conclusions derived from visual observations of the samples with the aid of a SEM microscope. The post-conservation Raman/FTIR analyses confirmed what was previously detected by visual observations of the samples with the aid of a SEM. The presence of a certain reagent was detected by observing if the internal structures of the wood were saturated with consolidant or rather empty. Through these observations it

was suggested if the reagent is present in the sample, in larger or smaller quantities.

These observations are described in detail in the following chapter.

The post-conservation Raman/FTIR analyses coincided with the conclusions from visual observations, and therefore, as explained earlier, the results were quantitative at some extent.

## CHAPTER VII

## RE-CONSERVATION PROCEDURES AND RESULTS

As explained above, the three different wood samples from the *Vasa*, waterlogged sample (WS), EDMA sample (ES), and PEG sample (PS), were divided into different sub-samples for analysis and re-conservation. From these divisions six sub-samples were selected to be re-conserved with three different procedures: (1) the method used by the Conservation Research Laboratory (CRL) using silicone oil and a crosslinker; (2) a MTMS treatment developed by Dr. Wayne Smith; and (3) a MTMS treatment variation developed by the author. Table 5 summarizes the different procedures applied to the sub-samples.

Table 5. Summary of the different procedures applied to the sub-samples.

Re-conservation procedure	Waterlogged wood sample	EDMA sample	PEG sample
Silicone oil	WS4	ES4*	PS5**
MTMS re-treatment	-	-	PS6
Author's MTMS re-treatment	-	ES3*	PS4**

\* The PEG extraction of these two samples was conducted in the *Vasa* Museum from September 2002 to June 2005. From June 2005 until June 2007 the samples were immersed in tap water (Almkvist et al. 2004).

\*\* The PEG extraction of these two samples was conducted by the author as explained later.

In this chapter, each of the results derived from the three re-conservation procedures is presented and described in detail. Each sub-sample result is presented with the corresponding re-conservation procedure applied. For each case, the macroscopic results are presented first, and the microscopic results presented later.

In order to evaluate the results of the different re-treatments, five physical parameters of the sub-samples were evaluated. The parameters were: color, texture, dimensional change, weight/size ratio, and microscopic status of the wood structure.

Differences in color were established by visual observations with the aid of a Munsell® Soil Color Chart (Munsell 1946). Linear measurements were controlled with the aid of a metric caliper and 3D modeling software Rhinoceros®. From each of the samples, linear measurements were taken of the longitudinal, radial, and tangential axis. The volume of each sample was recorded and calculated using 3D scanning technology. The numerical volume values of the samples were obtained with the aid of 3D modeling software Rhinoceros®. The microscopic status of the wood structure was observed by scanning electron microscope (SEM) techniques.

### **First Procedure: Silicone Oil Treatment**

Three sub-samples, waterlogged oak wood sub-sample (i.e., WS4), pine wood EDMA sub-sample (i.e., ES4), and pine wood PEG sub-sample (i.e., PS5), were conserved with silicone oil treatment as previously described.

In the case of the pine wood PEG sub-sample (i.e., PS5), the extraction of PEG was conducted before treatment with silicone oil. The original 1960s PEG has to be

removed from the samples in order to apply the silicone oil treatment. Therefore, the extraction of the 1960s PEG was conducted as follows.

The extraction of PEG was conducted by placing the sub-samples into a beaker with one liter of DI water, and placing the beaker inside a ventilated oven set at 60 °C. The melting point of PEG 4000 is 54-58 °C (Grattan and Clarke 1987); thus 60 °C was high enough to melt the PEG without damaging the wood structure. The DI water in the beaker was replaced every 24 hours. The water acquired a brownish color (Figure 40) due to the tannins naturally contained in the wood, the iron salts, and the sulfur compounds, as in other studies conducted with *Vasa* wood (Björdal and Nilsson 2007).



Figure 40. Different beakers of DI water after PEG extraction.

The PEG extraction process was monitored by measuring the differences in the immersed weight of the sub-samples throughout the entire process. When the immersed weight of the sub-samples stabilized for several days, the extraction of the PEG was considered to be complete. The immersed weight of the sample increased over time due to the fact that the PEG coming out from the wood and accumulating in the solution is replaced by water. The differences in the immersed weight during the entire process were documented and compiled in Figure 41.

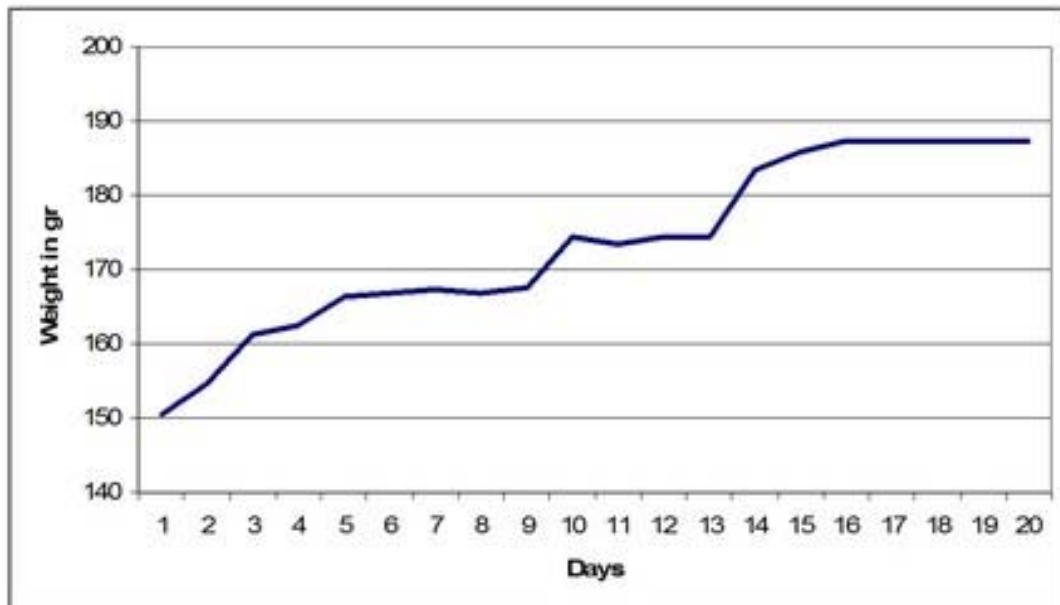


Figure 41. Weight variation of PEG sample (PS) during PEG extraction. The immersed weight of the sample increased overtime due the fact that the PEG coming out from the wood is replaced by water.

After the 1960s PEG was removed, the water was progressively extracted through solvent dehydration in sequential baths following the method described in Chapter II of this thesis (Figure 42).



Figure 42. Sub-sample WS4 during dehydration process.

Meanwhile, a fresh mixture of Dow Corning SFD1 silicone oil and MTMS 20% (by volume) was chosen to conserve the sample. After the dehydration, while thoroughly saturated with acetone, the sub-sample was transferred into a container with the polymer mixture. Throughout the acetone/polymer solution exchange the sample had a tendency to float due to the lower viscosity of the acetone. To ensure complete immersion of the



samples in the mixture, they were held below the solution's surface level with a plastic net and weighted by metal bolts to keep them submerged (Figure 43). Once the sub-sample was in the silicone oil mixture, the bath was placed under a low vacuum.



Figure 43. Container with the polymer mixture. Several sub-samples immersed into the polymer solution with the assistance of a plastic net and some improvised weights (bolts and nuts).

By applying vacuum, liquid acetone boils and evaporates to a gaseous state. In order to avoid uncontrolled boiling of the acetone, which could possibly damage the cellular structure of the samples, the vacuum was increased in progressive steps as follows: 12 Inches Hg / PSI maintaining this pressure for 30 minutes; 16 Inches Hg / PSI maintaining this pressure for 30 minutes; 18 Inches Hg / PSI maintaining this pressure for 48 hours; 22 Inches Hg / PSI maintain this pressure for 24 hours. After this period of time, the pressure was also dropped in progressive steps. The vacuum was gradually decreased with the purpose of avoiding damaging the structure of the sample due to an uncontrolled release of pressure. Finally, the samples were left in the polymer solution at ambient pressure for 24 hours more.

After the acetone/silicone oil displacement, the excess of polymer solution was left to drip by placing the sample on a metal screen for 24 hours. Then, the sample was soaked in MTMS in order to remove the excess silicone oil from cracks and crevices for a period of 30 minutes. Finally, the sample was slightly cleaned by wiping the surface with MTMS with the aid of a soft toothbrush and was dried with paper towels.

Finally, the sample was catalyzed through vapor deposition with dibutyltindiacetate (DBTDA) catalyst. The sample was placed into a sealed plastic bag along with a dish containing several grams of catalyst for a period of seven days at room temperature (Figure 44). After catalysis the samples were allow to sit in a fume hood for one day in order to eliminate residual catalyst vapors.



Figure 44. Catalysis of the samples. Three sub-samples during catalysis through vapor deposition inside a sealed plastic bag.

## **Results of the First Procedure: Silicone Oil Treatment**

### ***1 - Sub-Sample WS4, Waterlogged Wood Conserved with Silicone Oil***





#### Macroscopic Results of WS4 (Figure 45)

1. After conservation, the color of the sample was, in general terms, slightly lighter (i.e., it gained one degree of value at the Munsell® system) and slightly more intense or saturated (i.e., it gained one degree of value at the Munsell® system) from the original, as expected when compared from waterlogged wood to dry wood. Good color.
2. Good dry texture. The final texture was dry and non-sticky.
3. Shrinkage. Previous to treatment, the oak wood sample was waterlogged and hence swollen. After dehydration and re-conservation, dimensional changes were observed in the three lengths measured in the average range expected (Hoadley 1980:74; Hamilton 1996:26); therefore the results are considered good.
4. The sample lost 55.9% of its original waterlogged weight. After treatment, the ratio of weight/volume was slightly above the average in comparison with the value of oven-dry weight of fresh pine wood, thus highly satisfactory. The specific gravity of the sample was reduced by 52.7% after treatment. The final value was slightly above the average value of oven-dry weight of fresh oak (Hoadley 1990:51); therefore the results are considered excellent after its re-conservation with silicone oil (Table 6).



Figure 45. Macroscopic results of WS4. Three macroscopic photographs of oak sample (WS4) after being conserved with silicone oil: Upper left, tangential plane; upper right, cross-sectional plane; lower left, radial plane.

Table 6. Summary of the physical characteristics of oak sample (WS4). Before and after its re-conservation with silicone oil.

Color (Munsell® soil color chart reference # and color names)					
Pre-cons			Post-cons		
Exterior: 10YR 3/2; 10YR 4/4	Very dark grayish brown; Dark yellowish brown		Exterior: 10YR 4/3; 10YR 5/4	Dark brown; Yellowish brown	
Interior 10YR 2/1; 10YR 3/3	Black; Dark brown		Interior: 10YR 3/1; 10YR 4/1	Very dark gray; Dark gray	
Linear measurements					
Axis	Pre-cons	Post-cons		% change	
Longitudinal	118 mm	117.6 mm		- 0.3%	
Radial	24.6 mm	23.5 mm		- 4.6 %	
Tangential	32.6 mm	30.6 mm		- 6.5 %	
Weight					
Pre-cons (Waterlogged)	Post-cons (Silicone oil)	% change		Same volume average weight of <i>Quercus robur sp.</i>	
54.1 g	34.7 g	- 55.9 %		29.6 g	
Specific gravity					
Pre-cons (Waterlogged)	Post-cons (Silicone oil)	% change		Average Specific Gravity of <i>Quercus robur sp.</i>	
1.10 g/cm <sup>3</sup>	0.72 g/cm <sup>3</sup>	- 52.7 %		0.62 g/cm <sup>3</sup>	

#### Microscopic Results of WS4

A number of ESEM micrographs were taken before and after the conservation of the oak sample WS4. These different micrographs were taken to accurately document the status of the surface of the sample, before and after its re-conservation process. The surfaces of the sample were not cleaned via smooth cutting (Hoadley 1980:41). The reason for not cleaning the surface was to document the real status of the surface through micrographs. Due to the limitation of space, not all micrographs can be included in this thesis. Therefore, only two micrographs, representative of the status of the surface before and after the re-conservation process, are included below with the objective of describing and serving as an example of the condition of the sample's surface.

Two ESEM micrographs (Figure 46) of the oak sample taken before and after the treatment are below. As show in the micrographs, the cell structure of the oak was partially collapsed before the treatment. After treatment with silicone oil, the condition of the cell structure of the wood remained unchanged. However, the cell structure is saturated with polymer. Therefore, from a microscopic perspective the treatment result is poor.

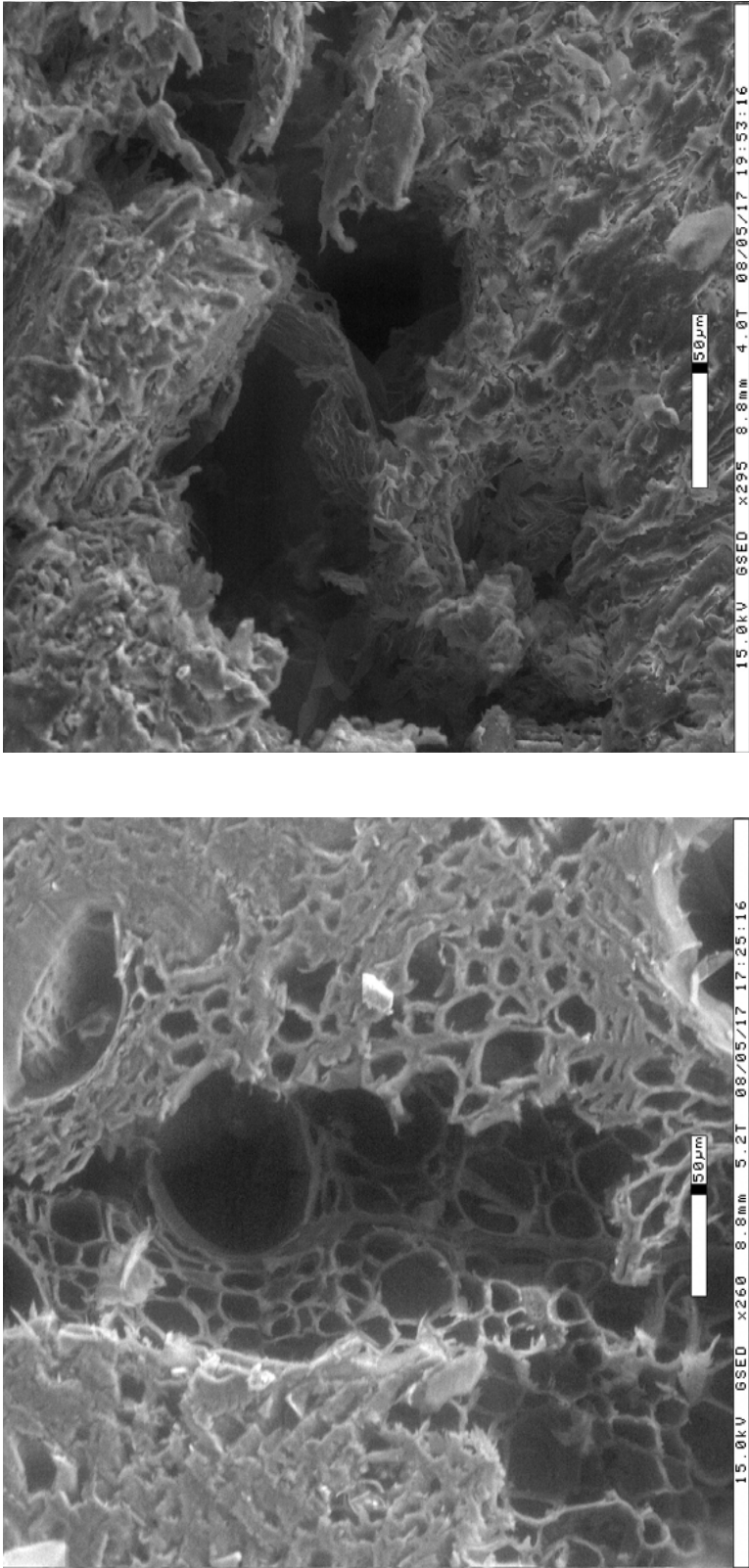


Figure 46. ESEM micrographs of oak sample (WS4). Left, before; right, after being conserved with silicone oils.



## ***2 - Sub-Sample ES4, EDMA Treated Wood re-Conserved with Silicone Oil***

The PEG and iron compounds of the pine sub-sample (i.e. ES4) were extracted through EDMA previously to this research.

### Macroscopic Results of ES4 (Figure 47)

1. Excellent color. After conservation, the color of the sample was, in general terms, slightly lighter (i.e., it gained one degree of value at the Munsell® system). The final sample has a color very similar to the original.
2. Average texture. The final texture was dry and non-sticky, yet it feels slightly oversaturated with polymer.
3. Shrinkage. Previous to treatment, the pine wood sample was waterlogged and hence swollen. After dehydration and re-conservation, dimensional changes were observed in the three lengths measured in the average range expected (Hoadley 1980:74; Hamilton 1996:26); therefore the results are considered good.
4. The sample lost 33.5% of its original waterlogged weight. After treatment, the ratio of weight/volume in comparison with the average value of oven-dry weight of fresh pine wood was very high. The specific gravity of the sample was reduced by 30% after treatment. Despite this considerable reduction, the final value was very high compared to the average value of oven-dry weight of fresh pine (Hoadley 1990:49); therefore the results are considered poor after its re-conservation with silicone oil (Table 7).

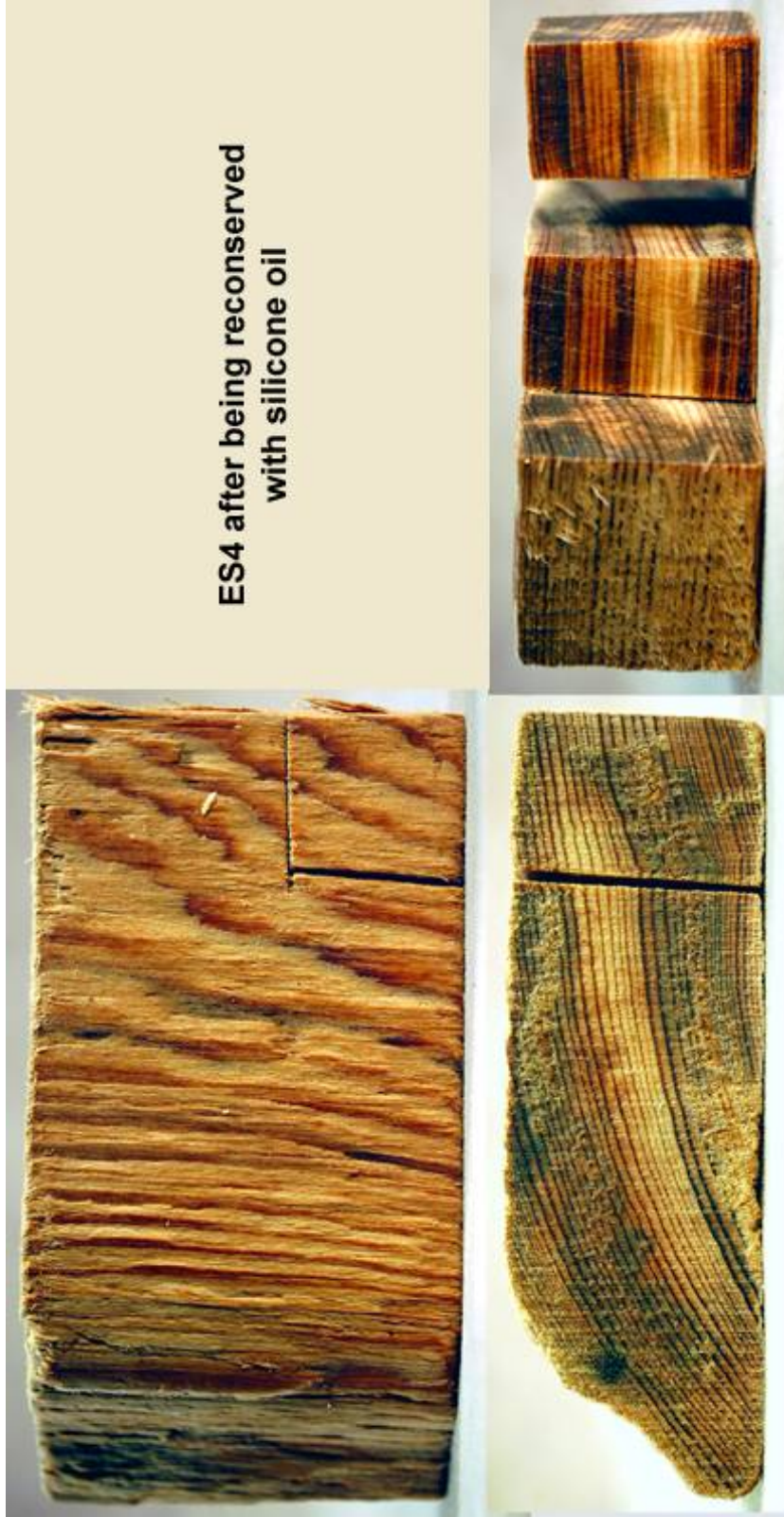






Figure 47. Macroscopic results of ES4. Three macroscopic photographs of pine sample (ES4) after being re-conserved with silicone oil: Upper left, tangential plane; lower left, cross-sectional plane; lower right, radial plane.

Table 7. Summary of the physical characteristics of pine sample (ES4). Before and after its re-conservation with silicone oil.

Color (Munsell® soil color chart reference # and color names)					
Pre-cons			Post-cons		
Exterior: 10YR 3/6; 10YR 4/6	Dark yellowish brown; Dark yellowish brown		Exterior: 10YR 4/6 10YR 6/6	Dark yellowish brown Brownish yellow	
Interior: 10YR 4/6; 10YR 7/4	Dark yellowish brown; Very pale brown		Interior: 10YR 5/6 10YR 8/4	Yellowish brown; Very pale brown	
Linear measurements					
Axis	Pre-cons	Post-cons		% change	
Longitudinal	55.7 mm	54.6 mm		- 2 %	
Radial	34.1 mm	33.2 mm		- 2.7 %	
Tangential	101.8 mm	98.7 mm		- 3.1 %	
Weight					
Pre-cons (Waterlogged)	Post-cons (Silicone oil)	% change		Same volume average weight of <i>Pinus sylvestris</i>	
174.7 g	130.8 g	- 33.5 %		74.6 g	
Specific gravity					
Pre-cons (Waterlogged)	Post-cons (Silicone oil)	% change		Average Specific Gravity of <i>Pinus sylvestris</i>	
1.04 g/cm <sup>3</sup>	0.80 g/cm <sup>3</sup>	- 30 %		0.46 g/cm <sup>3</sup>	

### Microscopic Results of ES4

A number of ESEM micrographs were taken before and after the conservation of the pine sample ES4. These different micrographs were taken to accurately document the status of the surface of the sample, before and after its re-conservation process. The surfaces of the sample were not cleaned via smooth cutting (Hoadley 1980:41). The reason for not cleaning the surface was to document the real status of the surface through micrographs. Due to the limitation of space, not all micrographs can be included in this thesis. Therefore, only two micrographs, representative of the status of the surface before and after the re-conservation process, are included below with the objective of describing and serving as an example of the condition of the sample's surface.

Two ESEM micrographs of the pine sub-sample taken before and after the treatment are below (Figure 48). As show in the micrographs, the cell structure of the pine was partially collapsed before the treatment. After treatment with silicone oil the condition of the cell structure of the wood remained unchanged. However, there is an excess amount of silicone oil filling the cell structure of the wood. Therefore, from a microscopic perspective the treatment result is poor.

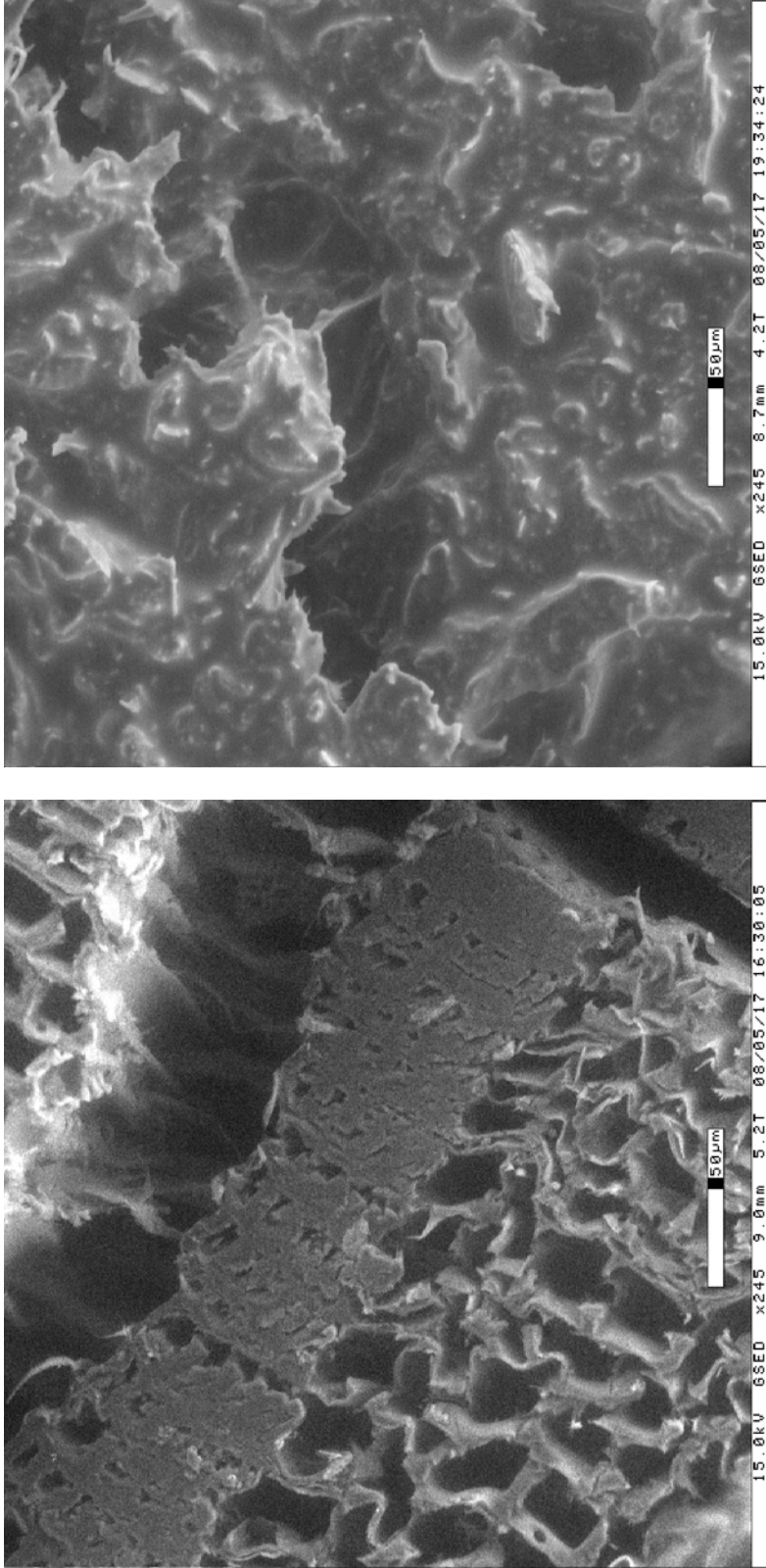


Figure 48. ESEM micrographs of pine sample (ES4). Left, before; right, after being re-conserved with silicone oils.

### ***3 - Sub-Sample PS5, PEG conserved Wood re-Conserved with Silicone Oil***

The pine sub-sample (i.e., PS5) was re-conserved by first a controlled extraction of PEG and subsequent re-treatment with the silicone oil procedure. The PEG extraction was conducted by the author following the procedure explained below.



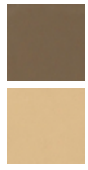

#### Macroscopic Results of PS5 (Figure 49)

1. After conservation, the color of the sample was, in general terms, slightly more intense or saturated (i.e., it gain one degree of value at the Munsell® system) from the original. Good color.
2. Good dry texture. The final texture was dry and non-sticky.
3. Shrinkage. Previous to the re-conservation treatment, the pine wood sample was completely impregnated with PEG and hence swollen. After re-conservation, dimensional changes were observed in the three lengths measured in the average range expected (Hoadley 1980:74; Hamilton 1996:26); therefore the results are considered good.
4. The sample lost 0.2% of its original PEG treated weight. After treatment, the ratio of weight/volume in comparison with the average value of oven-dry weight of fresh pine wood was very high. The specific gravity of the sample was increased by 2.2% after treatment. As a result, the final value was very high compared to the average value of oven-dry weight of fresh pine (Hoadley 1990:49); therefore the results are considered poor after its re-conservation with silicone oil (Table 8).



Figure 49. Macroscopic results of PS5. Three macroscopic photographs of pine sample (i.e. PS5) after being re-conserved with silicone oil: Upper left, tangential plane; lower left, radial plane; lower right, cross-sectional plane.

Table 8. Summary of the physical characteristics of pine sample (PS5). Before and after its re-conservation with silicone oil.

Color (Munsell® soil color chart reference # and color names)					
Pre-cons			Post-cons		
Exterior: 5Y 2.5/2; 10YR 5/1	Black; Gray		Exterior: 10YR 3/2; 10YR 5/3	Very dark grayish brown; Brown	
Interior: 10YR 4/2; 10YR 7/4	Dark grayish brown; Very pale brown		Interior: 10YR 4/4; 10YR 5/4	Dark yellowish brown; Yellowish brown	
Linear measurements					
Axis	Pre-cons		Post-cons		% change
Longitudinal	108 mm		107 mm		- 0.9 %
Radial	43.2 mm		41.6 mm		- 3.8 %
Tangential	34.5 mm		33.6 mm		- 2.6 %
Weight					
Pre-cons (PEG)	Post-cons (Silicone oil)		% change		Same volume average weight of <i>Pinus sylvestris</i>
87.6 g	87.4 g		- 0.2 %		45.4 g
Specific gravity					
Pre-cons (PEG)	Post-cons (Silicone oil)		% change		Average Specific Gravity of <i>Pinus sylvestris</i>
0.86 g/cm <sup>3</sup>	0.88 g/cm <sup>3</sup>		+ 2.2 %		0.46 g/cm <sup>3</sup>



### Microscopic Results of PS5

A number of ESEM micrographs were taken before and after the conservation of the pine sample PS5. These different micrographs were taken to accurately document the status of the surface of the sample, before and after its re-conservation process. The surfaces of the sample were not cleaned via smooth cutting (Hoadley 1980:41). The reason for not cleaning the surface was to document the real status of the surface through micrographs. Due to the limitation of space, not all micrographs can be included in this thesis. Therefore, only two micrographs, representative of the status of the surface before and after the re-conservation process, are included below with the objective of describing and serving as an example of the condition of the sample's surface.

Two ESEM micrographs of the pine sub-sample taken before and after the treatment are below (Figure 50). As shown in the micrographs, the cell structure of the pine was completely bulked with PEG before the treatment. After treatment with silicone oil, the condition of the cell structure of the wood remained unchanged. However, there is an excess amount of silicone oil filling the cell structure of the wood. Therefore, from a microscopic perspective the treatment result is from average to poor.

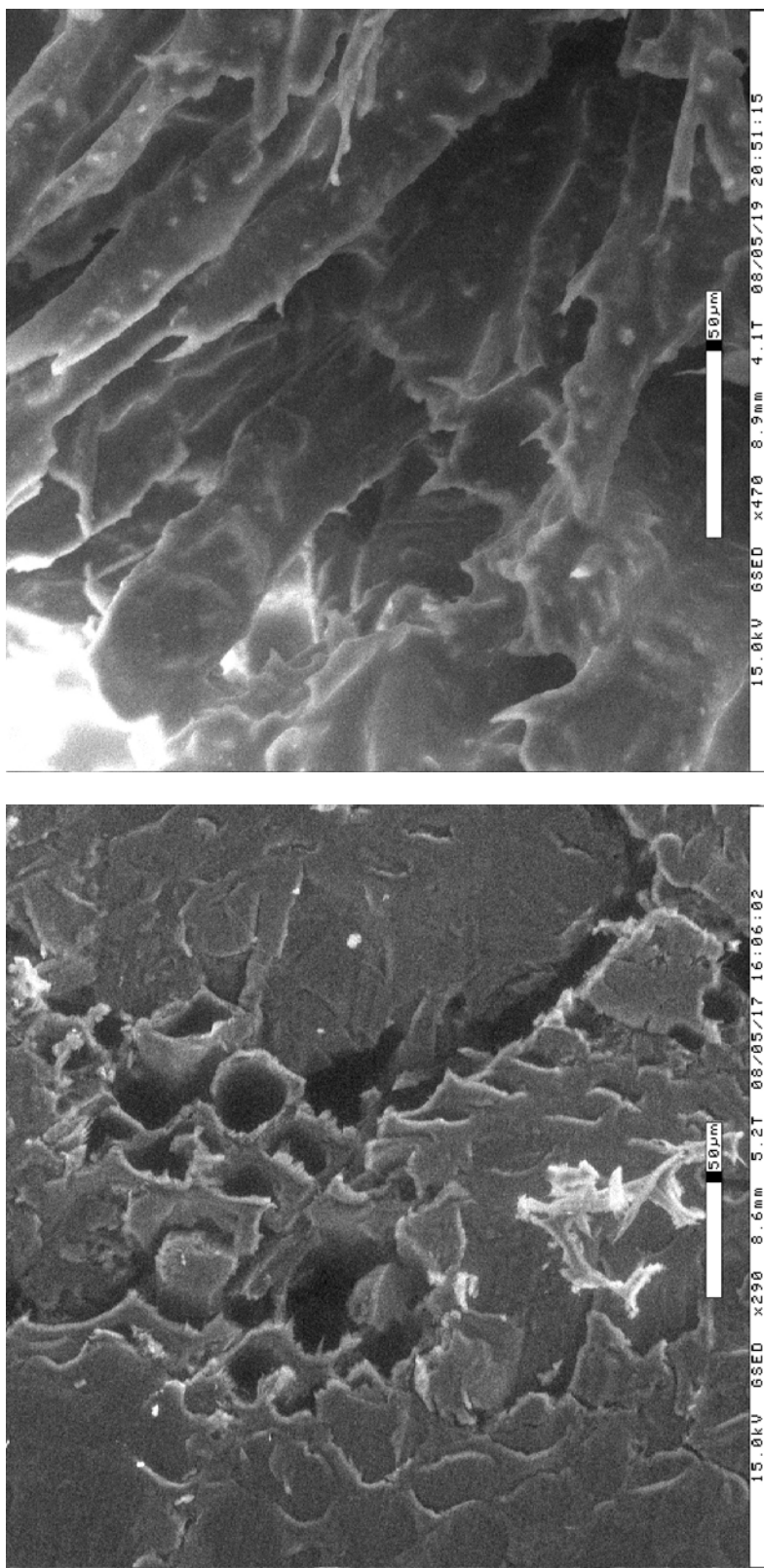


Figure 50. ESEM micrographs of pine sample (PS5). Left, before; right, after being re-conserved with silicone oil.

## **Second Procedure: MTMS re-Treatment Method**

This procedure was developed by Dr. Wayne Smith of TAMU as a re-treatment method for previously conserved artifacts by impregnation with PEG (Smith 1998, 2003:30-59). Dr. Smith's procedure consists of immersing a previously PEG-treated artifact in MTMS, a hydrolyzable multifunctional alkoxy silane polymer, at 70 °C. A complete explanation of the method can be found in Smith (2003:30-59; 1998). A 1960s PEG-treated pine wood sub-sample (i.e., PS6) was treated by Dr. Smith's MTMS re-treatment procedure.

Dr. Smith's procedure has two main goals: (1) to remove the non-essential PEG from the wood; and (2) use MTMS to polymerize (cross-link) this remaining PEG bonded to the wood structure cells' walls. These two goals are achieved with a single step: immersing the PEG treated artifact in MTMS at 70 °C. By removing the nonessential PEG and crosslinking the remaining PEG and cellular structure, stability to the cells of the wood would be provided, thus preventing shrinkage or collapse of the wood structure (Smith 1998; 2003:30-59).

In this study, the original PEG-treated sub-sample (i.e., PS6) was placed into a beaker with MTMS. The container was then covered tightly with aluminum foil to prevent the rapid evaporation of the MTMS. The beaker with the immersed sample was placed into a vented oven at 70 °C. The MTMS was replaced with fresh MTMS every 24 hours. After the fourth day of treatment, the MTMS was renewed every 48 hours. Throughout the process the temperature was maintained at 70 °C, at which the nonessential PEG is melted and extracted from the sample (Smith 1998; 2003:30-59).

The PEG extraction process was monitored by measuring the differences in immersed weight of the sub-sample throughout the entire procedure. When the immersed weight of the sub-sample was stable over several days, the extraction process of the PEG was considered to be concluded. The immersed weight of the sample increased over time due the fact that the PEG coming out from the wood and accumulating in the solution is replaced by MTMS. Once the PEG extraction was concluded, the beaker containing the sub-sample was removed from the oven and allowed to cool at room temperature. The sub-sample was then removed from the beaker and allowed to dry under a fume hood for 48 hours. Differences in weight during the process were documented and compiled in Figure 51.

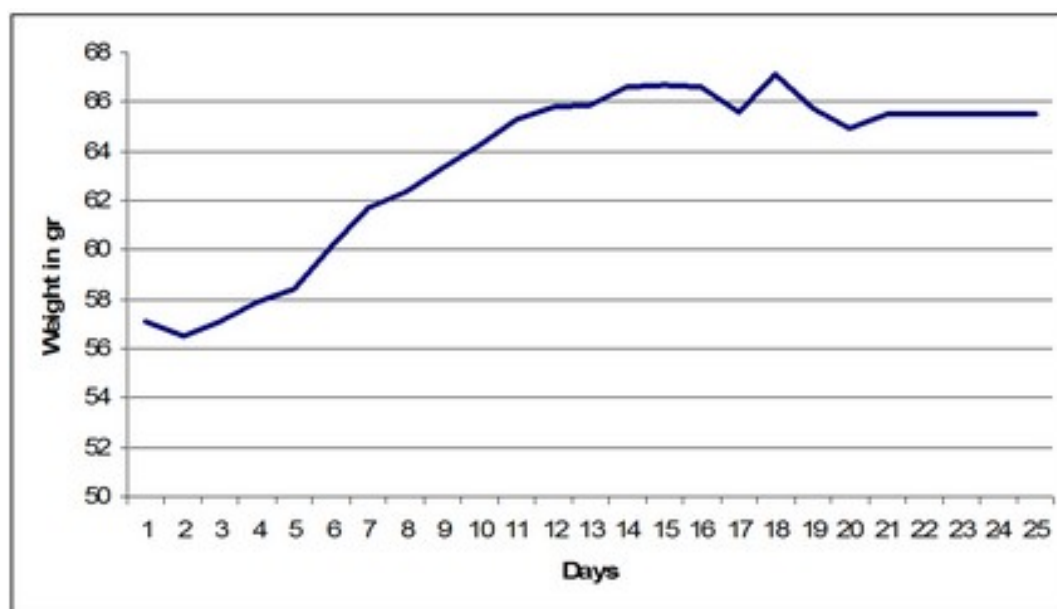


Figure 51. Weight variation of pine sub-sample (PS6) during MTMS re-treatment method. The immersed weight of the sample increased overtime due the fact that the PEG coming out from the wood is replaced by MTMS.

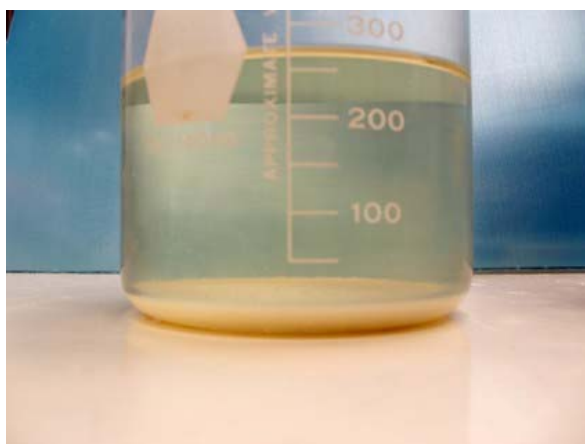


Figure 52. Beaker with used MTMS. Note the layer of extracted PEG on the bottom.

During treatment, the heat melted the PEG from the sample, resulting in migration to the exterior of the wood and concentration on the bottom of the beaker. The used MTMS acquired a slightly yellowish color, probably due to the impurities and debris captured in the PEG and certainly from the tannic acid of the wood (Figure 52). These two separate layers are the result of the different viscosity and polarity of MTMS and PEG. The former is hydrophobic (i.e., tending not to or incapable of dissolving in water) and the latter is hydrophilic (i.e., having a strong affinity for water). At room temperature, MTMS and PEG do not mix; thus when put together they form two separate layers in which PEG lies on the bottom due to its higher viscosity.

As a final step, the MTMS retained within the object is cured by vapor deposition catalysis with DBTDA catalyst as described earlier in the silicone oil procedure.

## **Results of Second Procedure: MTMS re-Treatment Method**

### ***4 - Sub-Sample PS6, PEG Conserved Wood re-Conserved with MTMS Treatment***

#### Macroscopic Results of PS6 (Figure 53)

1. After conservation, the color of the sample was, in general terms, slightly darker (i.e., it lost one degree of value at the Munsell® system) and slightly more intense or saturated (i.e., it gain one degree of value at the Munsell® system) from the original. Good color.
2. Average texture. The final texture was slightly waxy due to remaining PEG on the surface of the sample.
3. Shrinkage. Previous to the re-conservation treatment, the pine wood sample was completely impregnated with PEG and hence swollen. After re-conservation, dimensional changes were observed in the three lengths measured in the average range expected (Hoadley 1980:74; Hamilton 1996:26); therefore the results are considered good.
4. Despite the loss of PEG, the sample gained 10.5% from its original PEG-treated weight through the addition of MTMS. After treatment, the ratio of weight/volume in comparison with the average value of oven-dry weight of fresh pine wood was very high. The specific gravity of the sample was increased by 12.1% after treatment. As a result, the final value was very high compared to the average value of oven-dry weight of fresh pine (Hoadley 1990:49); therefore the results are considered unacceptable after its re-conservation with Dr. Smith's MTMS procedure (Table 9).

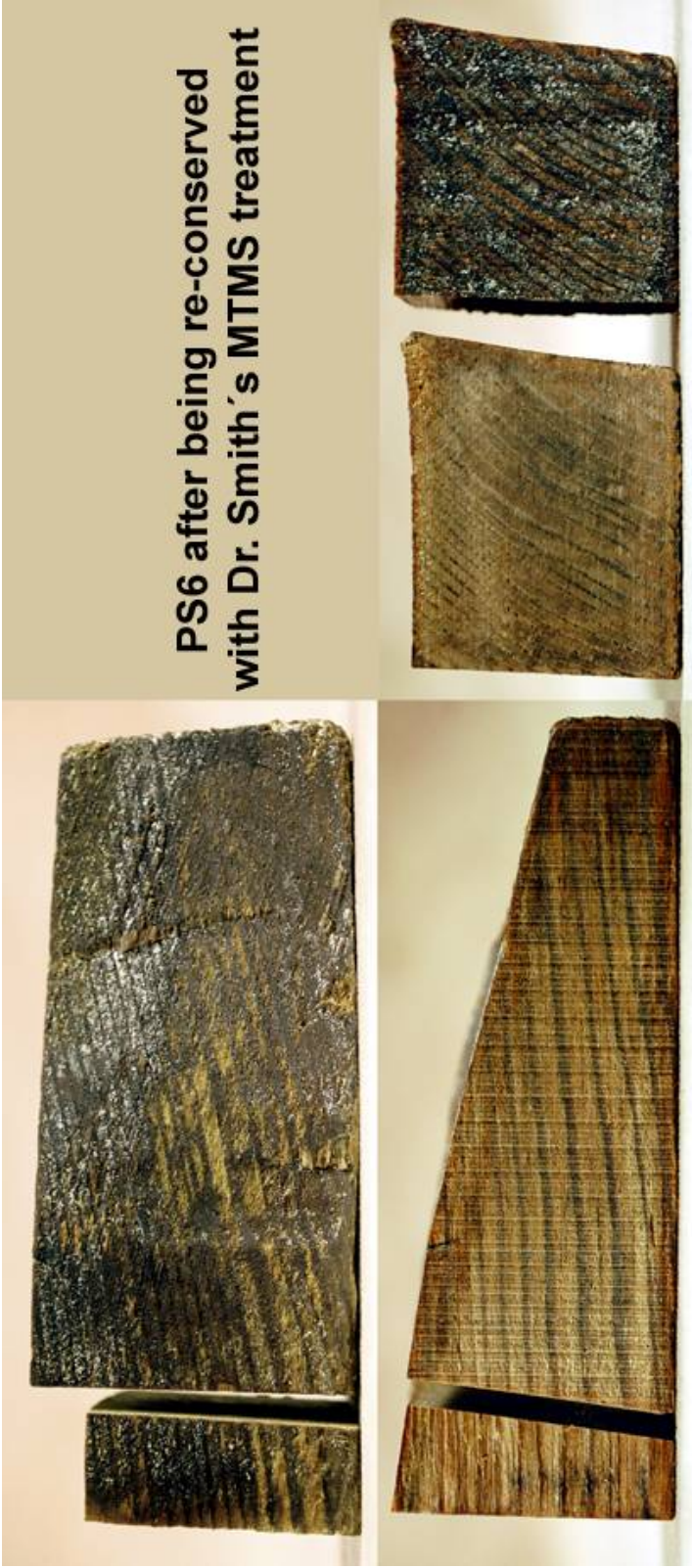






Figure 53. Macroscopic results of PS6. Three macroscopic photographs of pine sub-sample (i.e. PS6) after being re-conserved with Dr. Smith's MTMS procedure: Upper left, tangential plane; lower left, radial plane; lower right, cross-sectional plane.

Table 9. Summary of the physical characteristics of pine sample (PS6). Before and after its re-conservation with Dr. Smith's MTMS procedure.

Color (Munsell® soil color chart reference # and color names)					
Pre-cons			Post-cons		
Exterior: 5Y 2.5/2; 10YR 5/1	Black; Gray		Exterior: 10YR 2/2; 10YR 4/4	Very dark brown; Dark yellowish brown	
Interior: 10YR 4/2; 10YR 7/4	Dark grayish brown; Very pale brown		Interior: 10YR 5/3; 10YR 6/3	Brown; Pale brown	
Linear measurements					
Axis	Pre-cons	Post-cons		% change	
Longitudinal	85 mm	84.7 mm		- 0.3 %	
Radial	37.5 mm	36.5 mm		- 2.7 %	
Tangential	31.9 mm	30.2 mm		- 5.6 %	
Weight					
Pre-cons (PEG)	Post-cons (Smith's MTMS)	% change		Same volume average weight of <i>Pinus sylvestris</i>	
57.1 g	63.8 g	+ 10.5 %		29.4 g	
Specific gravity					
Pre-cons (PEG)	Post-cons (Smith's MTMS)	% change		Average Specific Gravity of <i>Pinus sylvestris</i>	
0.87 g/cm <sup>3</sup>	0.99 g/cm <sup>3</sup>	+ 12.1 %		0.46 g/cm <sup>3</sup>	



### Microscopic Results of PS6

A number of ESEM micrographs were taken before and after the conservation of the pine sample PS6. These different micrographs were taken to accurately document the status of the surface of the sample, before and after its re-conservation process. The surfaces of the sample were not cleaned via smooth cutting (Hoadley 1980:41). The reason for not cleaning the surface was to document the real status of the surface through micrographs. Due to the limitation of space, not all micrographs can be included in this thesis. Therefore, only two micrographs, representative of the status of the surface before and after the re-conservation process, are included below with the objective of describing and serving as an example of the condition of the sample's surface.

Two ESEM micrographs of the pine sub-sample take before and after the treatment are below (Figure 54). As shown in the micrographs, the cell structure of the pine was completely saturated of PEG before the treatment. After treatment with Dr. Smith's MTMS procedure, the cells of the wood were still filled with PEG (especially in the surface of the sub-sample). Therefore, from a microscopic perspective the treatment result is poor.

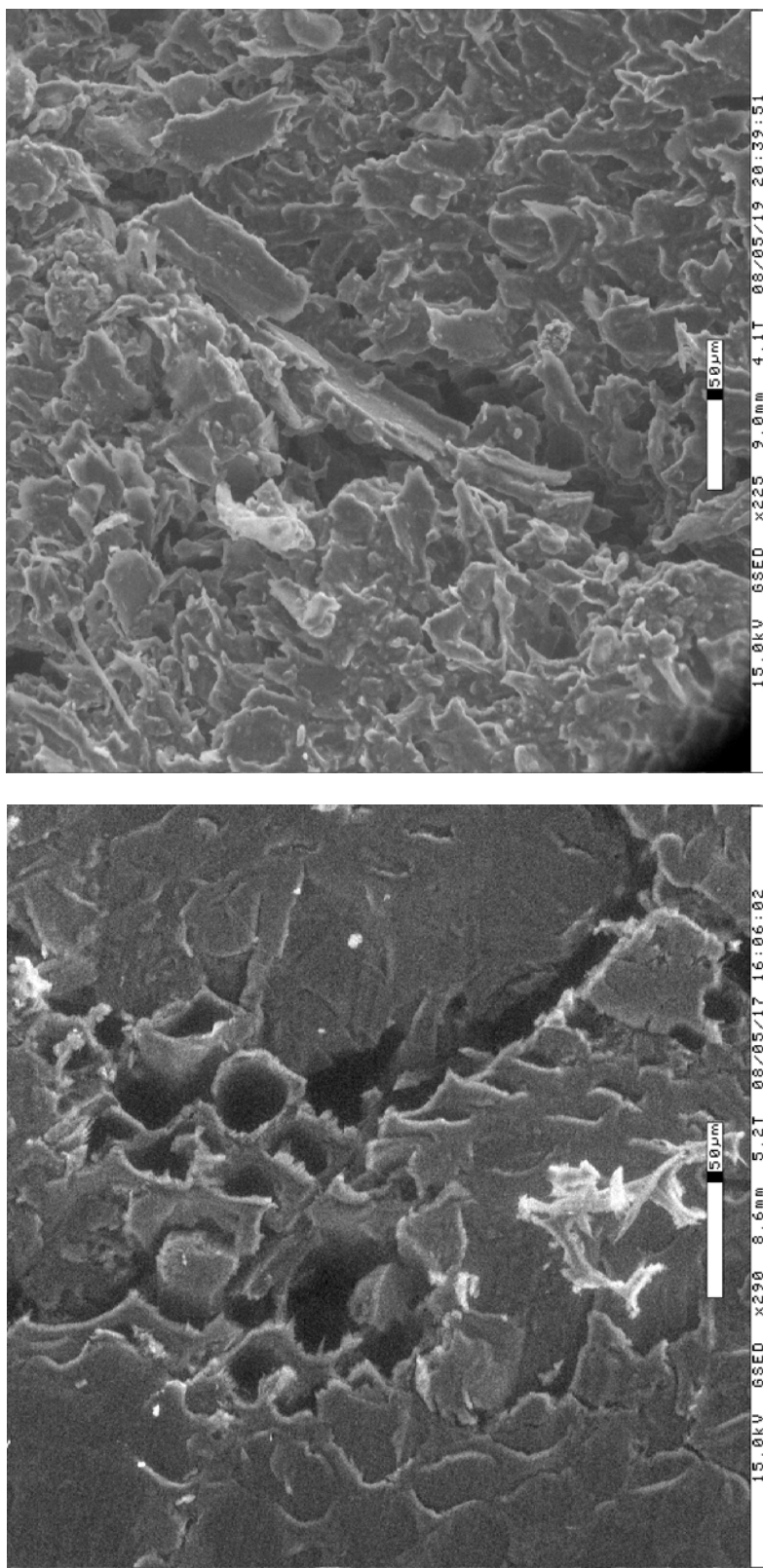


Figure 54. ESEM micrographs of the pine sample (PS6). Left, before; right, after being re-conserved with Dr. Smith's MTMS procedure.

### **Third Procedure: Author's Alternative MTMS re-Treatment Method**

The author developed an alternative MTMS re-treatment method combining two previous procedures. As explained earlier, Dr. Smith's MTMS procedure has two main goals: (1) to remove the non-essential PEG from the wood; and (2) to use MTMS to cross-link the remaining PEG in the wood structure. These two goals are achieved by one single step, immersing the PEG treated artifact in MTMS at 70 °C (Smith 1998, 2003:30-59). The author of this thesis expands upon Dr. Smith's study by achieving the same two main goals in separate steps instead of one.

Dr. Smith's idea of crosslinking the remaining PEG with MTMS was found to be successful. However, there are better approaches for extracting PEG from the sample than immersing the wood sample in MTMS at 70 °C. The different solubility of PEG and MTMS (i.e., the former hydrophilic, the latter hydrophobic) means they do not dissolve each other, resulting in the creation of two separate layers as previously seen in this chapter. Their different solubility does not facilitate the diffusion of PEG out of the wood structure; in fact, it makes it more difficult. Hence, for the extraction of PEG from the wood, better results can be achieved by using DI water, which has the same solubility of PEG, at 60 °C. This is the main difference between Dr. Smith's MTMS and the author's alternative MTMS re-treatment procedures.

The author's variation of the MTMS re-treatment method has four steps: (1) the PEG is extracted from the wood with heated DI water at 60 °C; (2) the remaining water in the sample is removed through solvent dehydration; (3) the sample is cross-linked with MTMS; and (4) the sample is catalyzed through vapor deposition.

The PEG extraction of the sub-samples (i.e., PS3, PS4, and PS5) was conducted following the same method explained earlier. However, the PEG extraction of the EDMA sub-sample (i.e., ES3) was previously conducted at the *Vasa* Museum (Almkvist et al. 2004).

Once the PEG was removed, the water of the sub-sample was extracted through progressive solvent dehydration. After the dehydration, the sub-sample was transferred into a beaker with fresh MTMS (while thoroughly saturated with acetone). The beaker with the MTMS and the sample were placed under a slight amount of vacuum for 24 hours. Then, the sample remained in the bath for a 24-hour period at ambient pressure. Finally, the sample was allowed to dry at room temperature under a fume hood for 48 hours. Finally, and to ensure total polymerization, the sample was catalyzed through vapor deposition with DBTDA as described earlier.

### **Results of Third Procedure: Author's Alternative MTMS re-Treatment Method**

#### ***5 - Sub-Sample ES3, EDMA Treated Wood re-Conserved with Author's MTMS***

##### ***Treatment***

The pine sub-sample (i.e., ES3), which PEG and iron compounds were previously extracted, was re-conserved with the author's MTMS procedure.


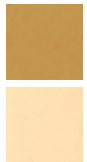


### Macroscopic Results of ES3 (Figure 55)

1. Average color. After conservation, the color of the sample was, in general terms, significantly lighter (i.e., it lost one degree of value at the Munsell® system) and slightly less intense or saturated (i.e., it lost one degree of value at the Munsell® system) from the original.
2. Poor texture. The final texture was somewhat dry and brittle.
3. Shrinkage. Previous to the re-conservation treatment, the pine wood sample was completely waterlogged and hence swollen. After re-conservation, dimensional changes were observed in the three lengths measured in the average range expected (Hoadley 1980:74; Hamilton 1996:26); therefore the results are considered good.
4. The sample lost 135.5% from its original waterlogged weight. After treatment, the ratio of weight/volume in comparison with the average same volume of oven-dry weight of fresh pine wood was very similar, hence too dry. The specific gravity of the sample was decreased by 136.1% after treatment. As a result, the final value was very similar compared to the average value of oven-dry weight of fresh pine (Hoadley 1990:49); therefore the results are considered poor after its re-conservation with author's MTMS procedure (Table 10).



Figure 55. Macroscopic results of ES3. Three macroscopic photographs of pine sample (ES3) after being re-treated with author's MTMS procedure: Upper left, tangential plane; lower left, radial plane; lower right, cross-sectional plane.

Table 10. Summary of the physical characteristics of pine sample (ES3). Before and after its re-conservation with author's MTMS procedure.

Color (Munsell® soil color chart reference # and color names)					
Pre-cons			Post-cons		
Exterior: 10YR 3/6; 10YR 4/6	Dark yellowish brown; Dark yellowish brown		Exterior: 10YR 6/6; 10YR 8/4	Brownish yellow; Very pale brown	
Interior: 10YR 4/6; 10YR 7/4	Dark yellowish brown; Very pale brown		Interior: 10YR 6/4; 10YR 7/3	Light yellowish brown; Very pale brown	
Linear measurements					
Axis	Pre-cons		Post-cons		% change
Longitudinal	52.6 mm		52.3 mm		- 0.5 %
Radial	33.8 mm		33.6 mm		- 0.5 %
Tangential	36.9 mm		36.8 mm		- 0.2 %
Weight					
Pre-cons (Waterlogged)	Post-cons (Author's MTMS)		% change		Same volume average weight of <i>Pinus sylvestris</i>
49.3 g	20.9 g		- 135.5 %		20.3 g
Specific gravity					
Pre-cons (Waterlogged)	Post-cons (Author's MTMS)		% change		Average Specific Gravity of <i>Pinus sylvestris</i>
1.11 g/cm <sup>3</sup>	0.47 g/cm <sup>3</sup>		- 136.1 %		0.46 g/cm <sup>3</sup>

### Microscopic Results of ES3

A number of ESEM micrographs were taken before and after the conservation of the pine sample ES3. These different micrographs were taken to accurately document the status of the surface of the sample, before and after its re-conservation process. The surfaces of the sample were not cleaned via smooth cutting (Hoadley 1980:41). The reason for not cleaning the surface was to document the real status of the surface through micrographs. Due to the limitation of space, not all micrographs can be included in this thesis. Therefore, only two micrographs, representative of the status of the surface before and after the re-conservation process, are included below with the objective of describing and serving as an example of the condition of the sample's surface.

Two ESEM micrographs of the pine sub-sample taken before and after the treatment are below (Figure 56). As shown in the micrographs, the cell structure of the pine was partially collapsed before the treatment. After treatment with MTMS the condition of the cell structure of the wood remained unchanged. However, the cells structure of the wood was free of any excess polymer. Therefore, from a microscopic perspective the treatment result is good.



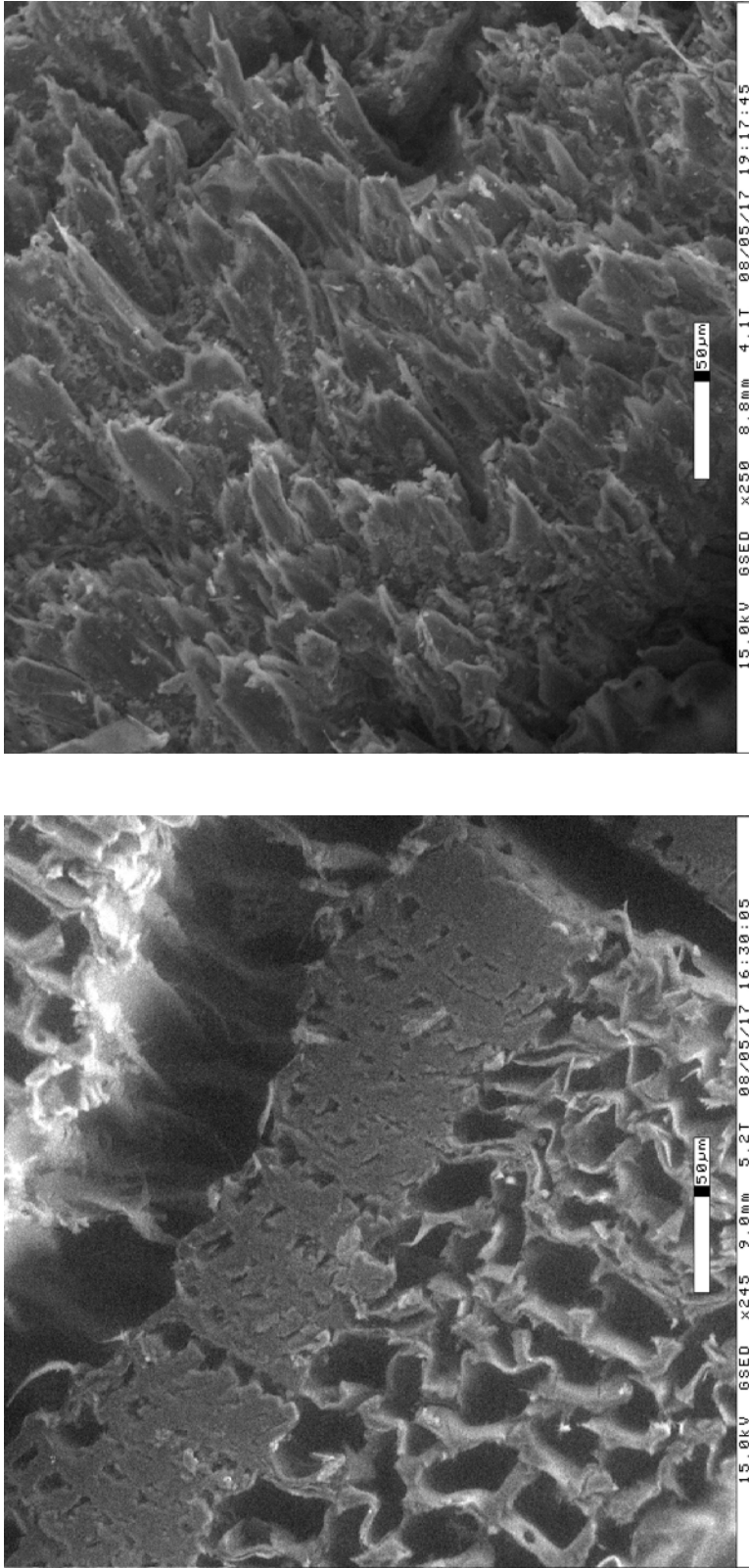


Figure 56. ESEM micrographs of pine sample (ES3). Left, before; right, after being re-conserved with author's MTMS procedure.

## ***6 - Sub-Sample PS4, PEG Conserved Wood re-Conserved with Author's MTMS***

### ***Treatment***

The pine sub-sample (i.e., PS4) was re-conserved through extraction of PEG and subsequent re-treatment with the author's MTMS procedure. The PEG extraction was conducted following the procedure explained above.





### **Macroscopic Results of PS4 (Figure 57)**

1. After conservation, the color of the sample was, in general terms, slightly darker (i.e., it lost one degree of value at the Munsell® system) and slightly more intense or saturated (i.e., it gain one degree of value at the Munsell® system) from the original. Good color.
2. Good dry texture. The final texture was dry and non-sticky.
3. Shrinkage. Previous to the re-conservation treatment, the pine wood sample was completely impregnated with PEG and hence swollen. After re-conservation, dimensional changes were observed in the three lengths measured in the average range expected (Hoadley 1980:74; Hamilton 1996:26); therefore the results are considered good.
4. The sample lost 23.2% of its original PEG-treated weight. After treatment, the ratio of weight/volume was above the average of oven-dry pine wood, thus satisfactory. The specific gravity of the sample was reduced by 19.4% after treatment. The final value was above the average value of oven-dry weight of pine (Hoadley 1990:49); therefore the results are considered good (Table 11).



Figure 57. Three macroscopic photographs of the pine sample (PS4) after being re-conserved with the author's MTMS treatment: Upper left, tangential plane; lower left, radial plane; lower right, cross-sectional plane.

Table 11. Summary of the physical characteristics of pine sample (PS4). Before and after its re-conservation with author's MTMS procedure.

Color (Munsell® soil color chart reference # and color names)					
Pre-cons			Post-cons		
Exterior: 5Y 2.5/2; 10YR 5/1	Black; Gray		Exterior: 10YR 4/4; 10YR 5/4	Dark yellowish brown; Yellowish brown	
Interior: 10YR 4/2; 10YR 7/4	Dark grayish brown; Very pale brown		Interior: 10YR 3/3; 10YR 6/4	Dark brown; Light yellowish brown	
Linear measurements					
Axis	Pre-cons		Post-cons		% change
Longitudinal	34.3 mm		34 mm		- 0.8 %
Radial	43.7 mm		41.4 mm		- 5.5 %
Tangential	33.6 mm		33 mm		- 1.8 %
Weight					
Pre-cons (PEG)	Post-cons (Author's MTMS)		% change		Same volume average weight of <i>Pinus sylvestris</i>
36.6 g	29.7 g		- 23.2 %		18.8 g
Specific gravity					
Pre-cons (PEG)	Post-cons (Author's MTMS)		% change		Average Specific Gravity of <i>Pinus sylvestris</i>
0.86 g/cm <sup>3</sup>	0.72 g/cm <sup>3</sup>		- 19.4 %		0.46 g/cm <sup>3</sup>

### Microscopic Results of PS4

A number of ESEM micrographs were taken before and after the conservation of the pine sample PS4. These different micrographs were taken to accurately document the status of the surface of the sample, before and after its re-conservation process. The surfaces of the sample were not cleaned via smooth cutting (Hoadley 1980:41). The reason for not cleaning the surface was to document the real status of the surface through micrographs. Due to the limitation of space, not all micrographs can be included in this thesis. Therefore, only two micrographs, representative of the status of the surface before and after the re-conservation process, are included below with the objective of describing and serving as an example of the condition of the sample's surface.

Two ESEM micrographs of the pine sub-sample taken before and after the treatment are below (Figure 58). As shown in the micrographs, the cell structure of the pine was completely saturated with PEG before the treatment. After treatment with MTMS, the cell structure of the wood is not collapsed. The cells were totally empty of any excess polymer. As a result, morphological characteristics of the wood structure are preserved in fine detail and identifiable. Therefore, from a microscopic perspective the treatment result is excellent.

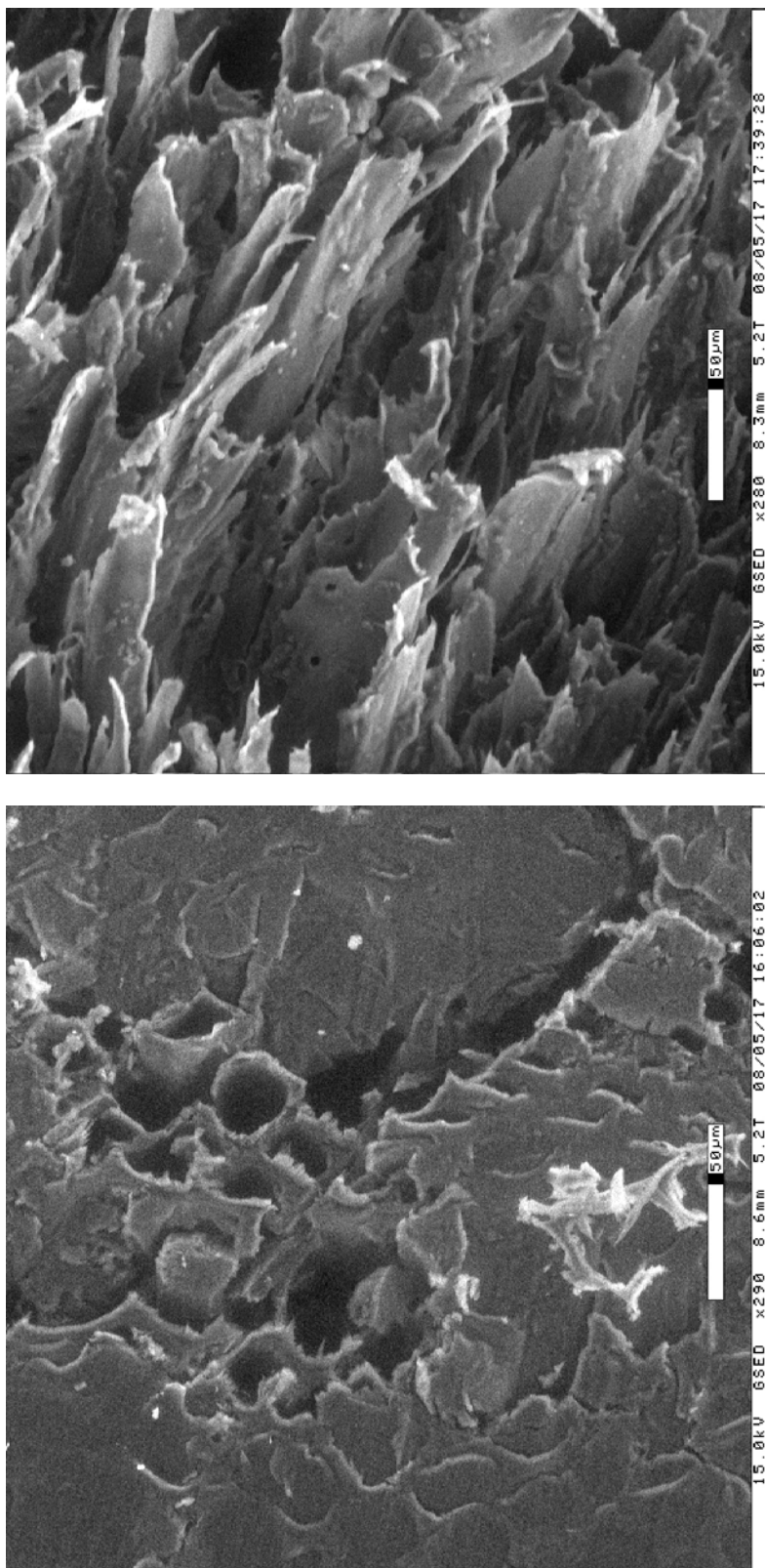


Figure 58. ESEM micrographs of pine sample (PS4). Left, before; right, after being re-conserved with the author's alternative MTMS treatment.

## CHAPTER VIII

### OVERALL EVALUATION OF THE RESULTS

#### **Evaluating the Results**

In order to evaluate the results of the different re-treatments, a matrix was created where five physical parameters of the sub-samples were evaluated by giving them numerical values. As explained above, several parameters were monitored: color, texture, dimensional change, weight/size ratio, and microscopic status of the wood structure. A numerical value was assigned to each one of the parameters as follows: Undesirable = 0, Poor = 1, Average = 2, Good = 3, Excellent = 4. The grades were compiled in the matrix in order to obtain an overall evaluation (Table 12).

Table 12. Evaluated parameters and grades of the six final sub-samples. Calculation key:

0 = Unacceptable; 1 = Poor; 2 = Average; 3 = Good; 4 = Excellent.

Re-conservation Treatment	Type of sample	Sub sample	Color	Texture	Dimensions	Weight	Specific Gravity	ESEM	Total
Silicone Oil method	Waterlogged	WS4	3	3	3	4	4	1	18
	EDMA	ES4	4	2	3	2	2	1	14
	PEG	PS5	3	3	3	1	1	1	12
MTMS method	PEG	PS6	3	2	3	0	0	1	9
Author's alternative MTMS	EDMA	ES3	2	1	3	1	1	3	11
	PEG	PS4	3	3	3	3	3	4	19



## **Silicone Oil Treatment**

### ***1 - Sub-Sample WS4, Waterlogged Wood Conserved with Silicone Oil***

Despite the poor microscopic outcome in which internal structures were saturated with polymer, the sample lost weight (-55.9%) and its specific gravity decreased (-52.7%), achieving an average value very close to that of air-dry oak. Therefore, the results for this sample were excellent. However, the results could be improved. The slightly wet texture and high weight due to the excess of polymer could be avoided by reducing the amount of silicone oil in the mixture employed to re-conservate the sample. Therefore, a mixture with less percentage of silicone oil and more percentage of MTMS would probably provide better results. In addition, the use of a polymer with a lower molecular weight than Dow Corning SFD1 (i.e., ~75 cSt) will give better results. Nevertheless, further tests should be conducted in order to establish a more suitable mixture. The process obtained an overall evaluation of excellent with a score of 18 (second-best result).

### ***2 – Sub-Sample ES4, EDMA Treated Wood re-Conserved with Silicone Oil***

The microscopic outcome was poor because the internal structures were saturated with polymer. Despite the fact that the sample lost weight (-33.5%) and its specific gravity decreased (-52.7%), the outcome was overweight higher than the average values of air-dry pine. Therefore, the results for this sample were average. However, as in the case of the previous sample, the results could be improved, and

further tests should be conducted in order to establish a more suitable mixture. The process obtained an overall evaluation of good with a score of 14 (third-best result).

### ***3 - Sub-Sample PS5, PEG conserved Wood re-Conserved with Silicone Oil***

In accordance with the poor microscopic outcome, in which internal structures were saturated with polymer, the sample barely lost weight (-0.2%), and its specific gravity increased (+2.2%), staying higher than the average values of air-dry pine. Therefore, the results for this sample were average. However, the results could be improved. The slightly wet texture and slightly high weight due to the excess polymer could be avoided. The results could be improved by reducing the amount of silicone oil in the silicone oil/MTMS mixture employed to re- conserve the sample. Therefore, a mixture with less silicone oil and more MTMS would probably offer better results. Nevertheless, further tests should be conducted in order to establish a more suitable mixture. The process obtained an overall evaluation of average with 13 (fourth position).

### **MTMS re-Treatment Method**

#### ***4 - Sub-Sample PS6, PEG Conserved Wood re-Conserved with MTMS Treatment***

As a result of several factors, the results were not satisfactory. The sample had a poor microscopic outcome, in which internal structures were saturated with polymer; the sample, despite having lost PEG, gained weight (+10.5%), and its specific gravity increased (+12.1%), high above the optimal. Therefore, the results for this sample were poor. As suggested by Dr. Smith, the results could be improved by eliminating the layer

of PEG formed on the exterior surfaces of the sample by wiping with lint-free cloths (Smith 1998, 2003). Due to the different solubility of PEG and MTMS, they create separate layers, and, in this case, PEG is deposited on the surface of the sample.

The increase in weight in the sample could have two hypothetical explanations: Nuclear Magnetic Resonance (NMR) spectrographic analysis conducted by Dr. Smith (Smith 2003) has demonstrated that silicone polymers are formed by the hydrolysis of the MTMS in an aqueous environment. Perhaps these new polymers were the reason for the increase in weight. Also, the 70 °C applied in the procedure could have broken the PEG 4000 polymer chains into smaller molecular weight PEG polymer chains. Hence, despite losing PEG, the sample increased its weight because the resulting PEG absorbed more atmospheric moisture from the ambient. Another hypothesis came from the fact that since PEG has been partially removed, void cavities have been created due to the absence of PEG. These void cavities increased the specific surface area (i.e., the total surface area per unit of mass). Before treatment the sample was less hygroscopic because the specific surface area was smaller. The fact that the PEG (which is hygroscopic) has not been totally removed, and the fact that the specific surface area has been increased, could lead to a situation in which the resulting sample is more hygroscopic. However, in order to prove any of these hypotheses, further analysis should be conducted. The results obtained in this study applying the MTMS treatment differ from the results obtained by Dr. Smith (Smith 1998, 2003). This discrepancy could be the result of many factors. Since only one sample was tested in this study, the results have to be considered in relative terms. Nevertheless, further analysis should be

conducted. Regardless, the process obtained an overall evaluation of average with 9 (sixth position).

### **Author's Alternative MTMS Treatment**

#### ***5 - Sub-Sample ES3, EDMA Treated Wood re-Conserved with Author's MTMS***

##### ***Treatment***

Despite the good microscopic outcome, in which internal structures were free of polymer, the sample lost too much weight (-135.5%); hence the outcome was extremely light weighted, and its specific gravity dramatically decreased (-136.1%), compared to that of oven-dried wood. Therefore, the results for this sample were average. The results could be improved. The dry texture and light weight of the sample could be avoided by either increasing the amount of silicone oil in the mixture employed to re- conserve the sample, or employing a higher molecular weight polymer. This higher percent of polymer will give elasticity and weight to the sample. Further tests should be conducted in order to establish a more suitable mixture. Regardless, the process obtained an overall evaluation of average with a score of 11 (fifth position).

#### ***6 - Sub-Sample PS4, PEG Conserved Wood re-Conserved with Author's MTMS***

##### ***Treatment***

As a result of several factors, the results were extraordinary. The sample had a excellent microscopic outcome, in which internal structures were free of polymer and it was possible to observe small diagnostic structural details of the wood; the sample lost

PEG, decreased its weight (-23.2%), and increased its specific gravity (-19.4%), staying slightly above the average values of air-dry pine. Therefore, the results for this sample were extremely satisfactory. Of the three re-conservation procedures tested in this study, based on the results this is the most suitable re-conservation method for wood previously conserved with PEG. The process obtained an overall evaluation of excellent with a score of 19 (best result).

## CHAPTER IX

## DISCUSSION

**Waterlogged Wood Conservation**

When something is recovered from a waterlogged environment, the first idea that an inexperienced person has is to let the finds air-dry. However this is not a good approach. It is true, however, that eventually materials have to be dry in order to be stored or displayed at museums, but this task has to be performed without jeopardizing the artifacts.

Waterlogged wood is a difficult material to deal with and very complex to conserve. The wood is very heavy due to the weight of the contained water but very soft and fragile due to the degradation process that it experienced. A detailed exposition of the particularities of waterlogged wood can be found in Grattan (1987:55-67).

Although the material looks like wood soaked with water, from the chemical and physical point of view, this material can not be defined as wood. The material that once was wood has lost many of its natural components. Water-soluble substances, such as starch and sugar, are the first to be leached from waterlogged wood, along with other bonding materials. With time, through hydrolysis, cellulose in the cell walls disintegrates, leaving only a lignin network to support the wood. Over a long period of time, even the lignin will break down (Hamilton 1996:26).

As a result of the disintegration of cellulose and lignin, spaces between the cells and molecules increase, and the wood becomes more porous and permeable to water,

absorbing it like a sponge. All of the deteriorated elements of the wood, including all cell cavities and intermolecular spaces, are filled with water. The remaining lignin structure of wood cells and the absorbed water preserves the shape of the wood. Waterlogged wood retains its shape as long as it is kept wet (Hamilton 1996:26). If the wood is exposed to air, the excess water evaporates, and the resulting surface tension forces of the evaporating water cause the weakened cell walls to collapse, creating considerable shrinkage and distortion (Grattam 1987:55).

The main challenge in waterlogged wood conservation is to dry the wood (i.e., extract the water within the wood) in such a way that subsequent collapse and shrinkage of the wood structure can be minimized or avoided.

Any conservation procedure for waterlogged wood should follow four ethical principles (Grattan and Clarke 1987:164). The procedure should stabilize the shape and size of the object to those of the waterlogged condition as closely as possible (Barbour and Leney 1981:208-225). The conservation procedure should give durability to the material composing the objects (Brorson-Christensen 1970). The materials used as consolidants in any procedure should be reversible. No process should be carried out that cannot, at some later stage, be altered and ideally be possible to return the object to the waterlogged condition for re-treatment. Finally, minimum intervention is desirable on a treatment that interferes with or modifies the wood to the least extent (Grattan and Clarke 1987:164).

Five approaches can be followed to achieve the objective of dry the wood while trying to avoid the collapse and shrinkage of the wood structure: impregnation, bulking,

solvent dehydration, freeze-drying, and slow drying (Grattan and Clarke 1987:165-167).

These approaches were recently increased by the addition of a new technique:

supercritical drying.

### ***Impregnation***

Impregnation has the aim of filling all the spaces (i.e., the lumina, cell wall capillaries, and microcapillaries) within the wood with a chemically inert material that provides structural support and lends mechanical strength to the object. Impregnation also replace the waterlogging water so that the tension effects of drying (which lead to collapse) are prevented and drying stresses are avoided. The impregnant remaining in the lumina physically prevents any distortion of the wood cells. The impregnant can also act as a moisture-absorbing buffer to reduce the effects of changes in relative humidity. The impregnation agent should solidify in the lumina before the drying of the wood commences (Grattan and Clarke 1987:165).

Several materials have been used for this purpose: rosin (McKerrell and Varsanyi 1972:17:111-25; Bryce, McKerrell, and Varanyi 1975; Fox 1987), sucrose (Parrent 1983, 1985; Hoffmann 1990a, 1993), but probably the most popular is polyethylene glycol (PEG). Total impregnation with PEG is probably the most widespread conservation procedure for the conservation of large waterlogged wood artifacts (Barkman 1965, 1967, 1975, 1976; Brorson-Christensen 1970; De Jong 1978, 1981; Grattan 1981, 1982; Hoffmann 1984, 1986, 1988, 1990b, Grattam and Clarke 1987; Håfors 1990, 2001; Jones and Rule 1990; Jones et al. 2003). Total impregnation with



PEG was the method chosen to conserve the *Vasa* hull and the majority of the associated waterlogged wood artifacts (Barkman 1965, 1967, 1975, 1976; Håfors 1998, 2001). As explained above, the philosophy behind this approach is to replace the water within the wood with PEG, a water-soluble synthetic wax. Once the water has been replaced by PEG, it fills all cavities of the wood, conferring mechanical strength (Figure 59).

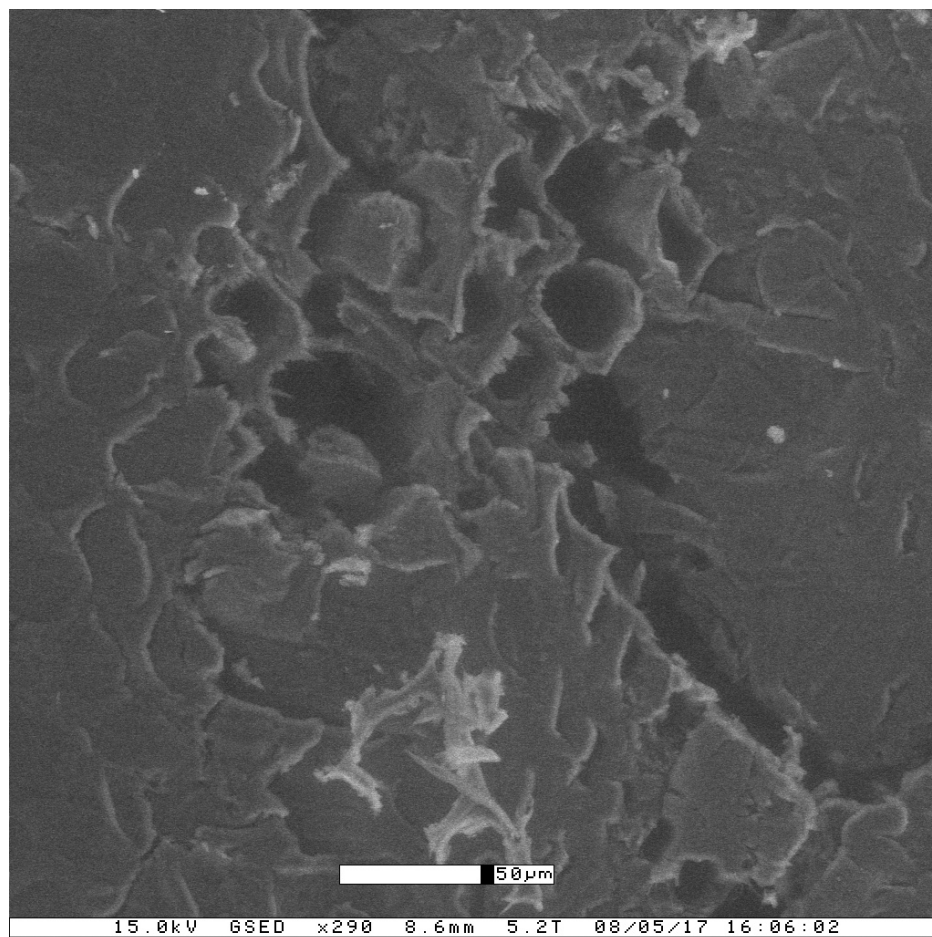


Figure 59. ESEM micrograph of PEG treatment. Pine sample (PS2) with the original 1960s PEG treatment. Note that the PEG completely fills the interior of the cellular structure of the wood.

Impregnation techniques present some problems. Complete filling of the lumina may be impossible to achieve because of the inherent impermeability of the wood. The degree to which the cell wall is penetrated is an important factor. If poor penetration occurs, the cell walls may still respond to humidity variations, whereas the impregnant may not, and consequently stress can develop leading to slow cracks. Osmotic collapse may occur, if an impregnant such as PEG, cannot pass through a membrane that the solvent may pass through. This phenomenon occurs in wood with different degrees of degradation. To avoid this problem, a two-step method, which employ mixtures of low molecular weight PEG and high molecular weight PEG, was developed and successfully applied (Hofmann 1984, 1986, 1988, 2001; Jones and Rule 1990; Jones et al. 2003). In this two-step method, low molecular PEG is first used to bulk the cell walls, and then high molecular weight PEG is used to impregnate the lumina.

Some of the inconveniences of total impregnation with PEG are the expensive price of the polymer, the use of special installations, and the duration of the treatments. Also, the tendency of the solid impregnant to change with time, as it happens with PEG that could absorb water and migrate. Finally, impregnation treatments leave the wood very heavy (i.e., the weight of the artifact increases drastically) and often unnatural in appearance (Grattan and Clarke 1987:165). A more detailed description of the impregnation method with PEG and its historical development can be found elsewhere (Grattan and Clarke 1987:164-206).

### ***Bulking***

This second approach is based on completely filling the micropores within the cell wall, strengthening the cell walls and thus becoming more resistant to collapse. Shrinkage of the wood is also reduced since the normal absorption and desorption of water by the cell wall is essentially eliminated. The advantages of cell-wall bulking rather than full impregnation are that the amount of bulking agent required is small and soaking periods may be quite short since only the cell walls are to be filled. Low molecular weight PEG, sugars, and vinyl monomers subsequently polymerized may be considered bulking agents. Bulking treatments leave the wood light in weight and natural in color (Grattan and Clarke 1987:165-166). A more detailed description of the different bulking methods can be found elsewhere (Grattan and Clarke 1987:164-206). Bulking is an inexpensive method that provides good results if performed properly.

### ***Solvent Dehydration***

The philosophy behind this approach is to replace the water with a non-aqueous solvent. Water has a remarkably high surface tension of  $0.073 \text{ N m}^{-1}$ . The elevated surface tension of water that makes that capillarity tension forces is considerably large; if the drying process is not controlled these forces will lead to the collapse of the wood structure. By simply progressively replacing all the water with ethanol, acetone, and diethyl ether with surface tensions of  $0.023$ ,  $0.024$ , and  $0.017 \text{ N m}^{-1}$  respectively, the capillarity forces are reduced, hence avoiding subsequent collapse. The solvent is finally

removed from the wood by simple evaporation, due to the high vapor pressure and a low boiling point.

The use of a non-aqueous solvent also allows to the introduction of resins, vinyl monomers, or, as in this study, alkoxy silanes. Common non-aqueous solvents, such as ethanol and acetone, have viscosities substantially lower than water. Diffusion and permeation rates are directly related to viscosity. In a media with lower viscosities than water, rates of diffusion and permeation are enhanced and therefore the impregnation period may be shorter (Grattan and Clarke 1987:166).

Solvent dehydration will allow the addition of camphor. Camphor can be used to impregnate the wood by filling up all its cavities. Due to the high vapor pressure and a low boiling point of camphor, it will sublime very slowly (i.e., goes directly from solid state to gas) preventing collapse and shrinkage of the wood structure (Hamilton 1996:30-31).

Non-aqueous solvents have the disadvantage that they represent serious fire and toxicity hazards, especially for acetone and diethyl-ether. Also, some minimal contraction takes place (Grattan and Clarke 1987:166). But on the other hand, solvent dehydration and the use of camphor are two relatively inexpensive methods that are able to dry waterlogged wood with minimum collapse and minimal shrinkage.

### ***Freeze-Drying***

Freeze-drying takes advantage of the physical process of sublimation. The water of the wood is frozen, and later, with the assistance of a freeze dryer, the ice formed is

sublimated (i.e., transformed into vapor with no intermediate liquid phase). By removing the water by direct conversion from the solid to the gas phase, the structure of the wood remains strong and intact during the drying, and the forces of capillary tension are eliminated (Grattan and Clarke 1987:166). A more detailed description of the freeze-dry method can be found elsewhere (Ambrose 1970, 1972, 1975, 1976; Biek and Cox 1975; McCawley et al. 1981; Watson 1981, 1987, 1996, 2004).

However, with waterlogged wood several complicating factors come into play, which make it difficult to conceive and control what takes place during the process. Studies have shown that water absorbed by the cell wall may not freeze. (Nanassy 1978; Flyate and Grunin 1974) This is usually referred to as the bound water.

Freeze-drying removes water from the lumina before the water evaporates from the cell wall. It stops collapse but allows shrinkage to take place. Thus, drying stress results, and cracking occurs. A further effect is that by freezing, water expands volumetrically by 9%. This phenomenon could be drastically reduced by using flash-freezing. For relatively intact waterlogged wood, serious cracking will occur. For highly degraded wood this phenomenon will be less important due to the increased plasticity of the wood (Grattan and Clarke 1987:167).

Nevertheless, by avoiding the liquid phase, collapse is prevented to a great extent, yet the result is an extremely dry wood that can be very brittle due to the state of degradation (Figure 60).

Some of the problems of the basic freeze-drying treatment were improved by first bulking the wood with low molecular weight PEG and then freeze-drying the bulked

samples (Rosenquist 1975; Grattan 1982:133; Watson 1987, 1996, 2004; Grattan and Clarke 1987:173; Cook and Grattan 1990).

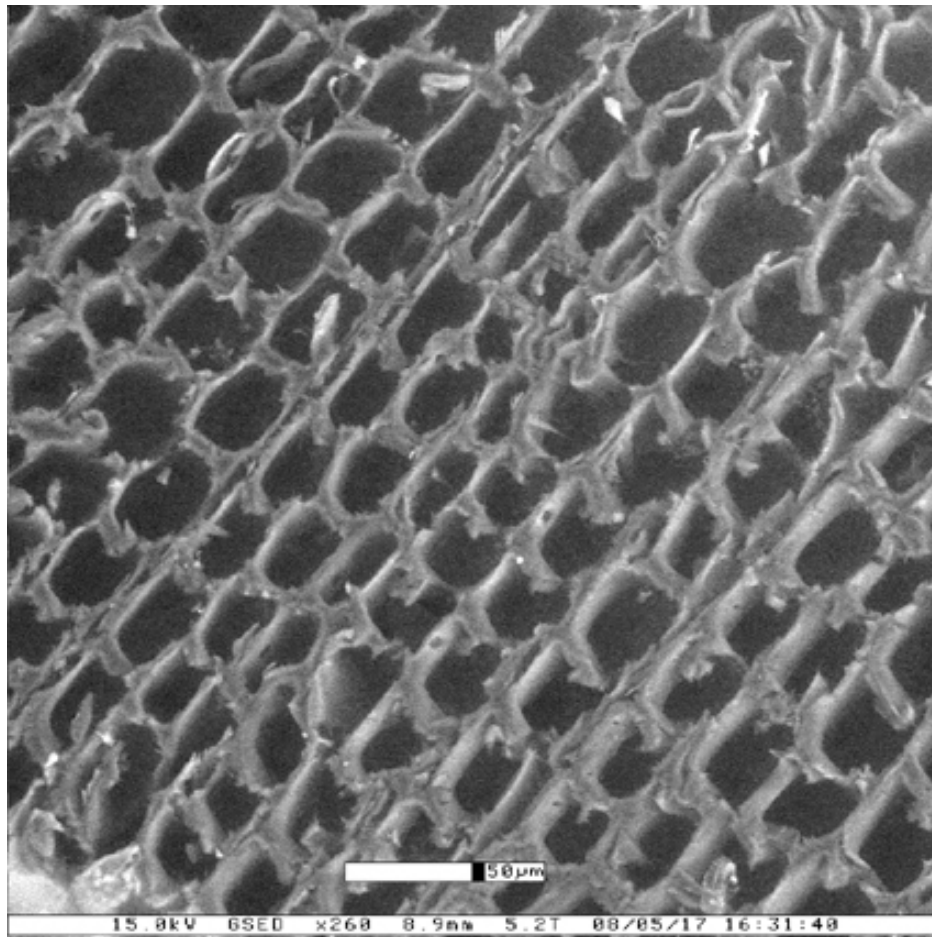


Figure 60. ESEM micrograph of pine sample (ES) after being freeze-dried. Note that the structures of the wood are totally empty, yet the cellular structure is maintained.

Despite this improvement, the excessive drying resulting from sublimation and the hygroscopic nature of PEG make freeze-dried wood hygroscopic in excess. The wood is highly affected by relative humidity changes and, therefore, should be stored and displayed under controlled environmental conditions. Other important inconveniences are the high cost of the freeze-dryer equipment and the degree of

expertise necessary to correctly perform this procedure. A more detailed description of the different freeze-drying techniques and their historical development can be found elsewhere (Grattan and Clarke 1987:164-206).

### *Slow Drying*

A useful way of seasoning green wood is to dry it slowly. The moisture can be redistributed as evenly as possible during the slow drying, reducing the drying stresses. Drying stresses are caused by the greater shrinkage of the outer surfaces of the wood, which dries first, compared to the interior, which loses water more slowly. The interior of the wood remains in an expanded condition longer. Considerable pressure on the interior (i.e., compression) can build up, which is largely alleviated either by collapse of interior cells or by checking of the outer zone. Slow drying may be of some benefit to waterlogged wood if drying stresses due to shrinkage will be alleviated. It has been suggested that collapse cannot be prevented for several reasons: The free water cannot redistribute itself because of the forces of surface tension and the lack of bubbles (Grattan and Clarke 1987:167); by the uneven distribution of moisture (Hawley 1931). However, controlled air drying of waterlogged wood has been performed with satisfactory results, at least with some specific types of wood (Schweizer et al. 1984). It is also necessary to mention the inexpensiveness of this method.

### *Supercritical Drying*

The supercritical drying technique avoids collapse and shrinkage caused by the tensions of drying effects or osmotic collapse from the misuse of consolidants. It has been the standard method for preparing samples for electron microscopy for many years. The technique does not require the use of consolidants and satisfies the conservation ideal of minimal intervention.

Supercritical drying process avoids the problems associated with the phase changes encountered in the other methods. As in the freeze-drying technique, supercritical drying uses the physical characteristics of certain substances in order to dry the wood without collapse or shrinkage. Above a certain critical temperature, fluids cannot be liquefied by compression. In the simplest case, the temperature and pressure are changed so that the liquid in the material is above its critical temperature. This must be carried out without crossing the liquid/vapor phase boundary. Above the critical temperature the fluid can be removed by decompression without any possibility of a liquid phase being formed, as long as the temperature is not allowed to fall. As no phase boundaries are crossed, no drying stresses are encountered.

The experimental results demonstrated the efficiency of the method, the reversibility of the technique, and the environmental stability of the wood conserved. However, as in the case of the freeze-drying technique, important inconveniences are encountered. The resulting wood is extremely dry, and further measurements have to be implemented for its proper storage or exhibition. Also, the elevated cost of the equipment and the high degree of expertise necessary for conducting the procedure are



two factors that limit the use of this procedure to research institutions, universities, or significant museums.

This technique has been implemented for the conservation of waterlogged archaeological wood in recent years, and a more detailed description can be found elsewhere (Kaye et al. 2000; Teshirogi et al. 2001; Schindelholz 2007).

### *Alkoxysilanes*

Re-conservation with alkoxysilanes is the fusion of two approaches: solvent dehydration and consolidation. The main principle is similar to the other consolidation techniques: the incorporation of an agent into the wood that consolidates and confers mechanical strength while the water is removed (Grattan and Clarke 1987). Silicone oils act as a consolidant, creating a three-dimensional protective film of material over and in the structures of the wood; it confers plasticity and structural strength without filling the hollow cellular structures of the wood.

When the silicone polymer comes into physical contact with any organic material, in this case wood, it creates a protective film. The alkoxysilanes molecules in contact with the cell walls of the wood react by establishing covalent chemical bonds. Those molecules will remain adhered to the object, and they cannot be removed. This chemically bonded polymer molecule embodies what could be called the “essential polymer.” Only the free-flowing or “nonessential polymer” (i.e., the one that did not form chemical bonds with the material) can be removed from the material by draining, rinsing, and cleaning before the catalysis of the polymer.

After the removal of the nonessential polymer, the essential polymer has to be polymerized through catalysis. Once the essential polymer is catalyzed, it forms a film that protects the wood. The material's structure is coated by the formation of a hard, yet flexible, non-reactive film that inhibits the treated material from further degradation. The material being coated with silicone polymer is *plasticized* on a microscopic scale.

If the silicone oil procedure is conducted properly, the amount of silicone oil retained in the object is negligible. The essential silicone polymer coats the surface of the structures of the wood without filling hollow structures of the wood. The polymer film's thickness is in the scale of micrometers, and can only be detected on a microscopic scale with the aid of scanning electron microscopy (Figure 61).

Because of the extreme thinness of the film that coats the wood, the physical characteristics (i.e., color, texture, weight) of the treated wood become very similar to those of the original wood. Without the aid of microscopic analysis, this polymer film is hardly detectable by organoleptic analysis (i.e., perceived by a sense organ).

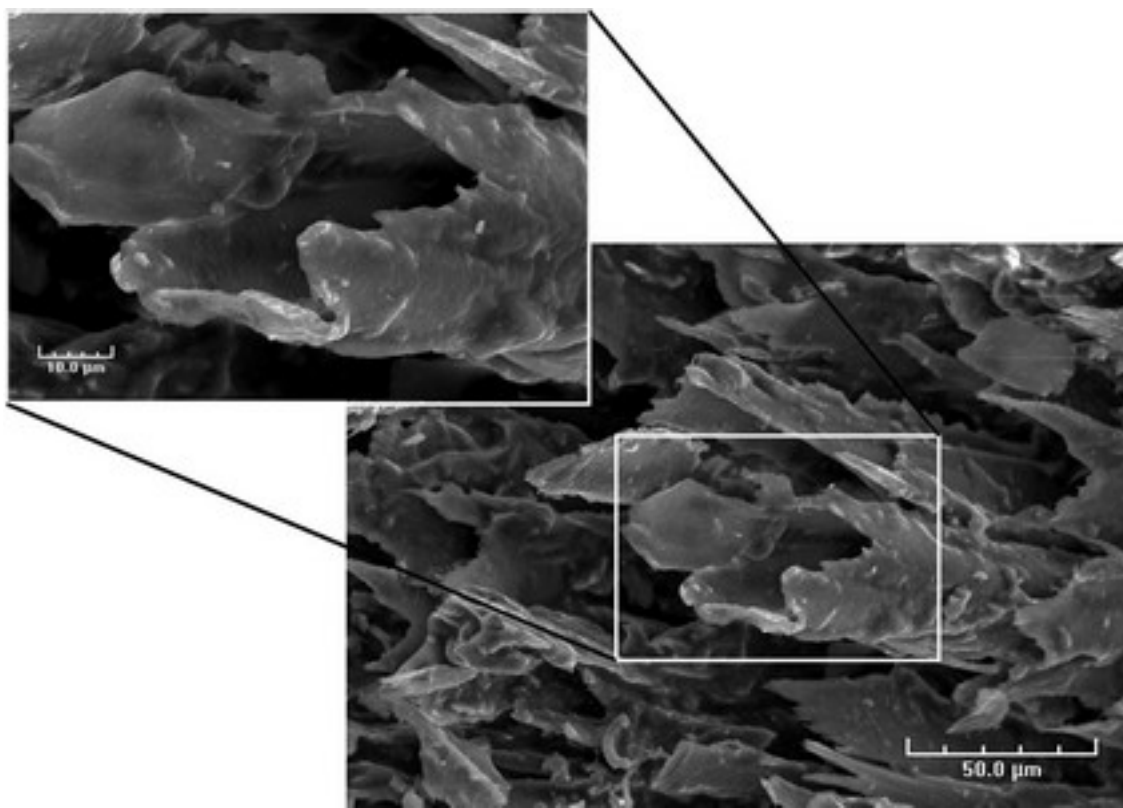


Figure 61. Two SEM micrographs of pine sample (PS4). The micrographs were taken after being re-conserved with author's MTMS procedure. Note the thinness of the silicone polymer coating.

Despite the thinness of the polymer film, it is able to maintain the conserved material's three-dimensional structure without collapse, shrinkage, or warping. This is because once the silicone is polymerized, it creates a highly cross-linked, stable, and flexible three-dimensional polymer matrix that supports and confers mechanical strength to the conserved wood structure (Figure 62).

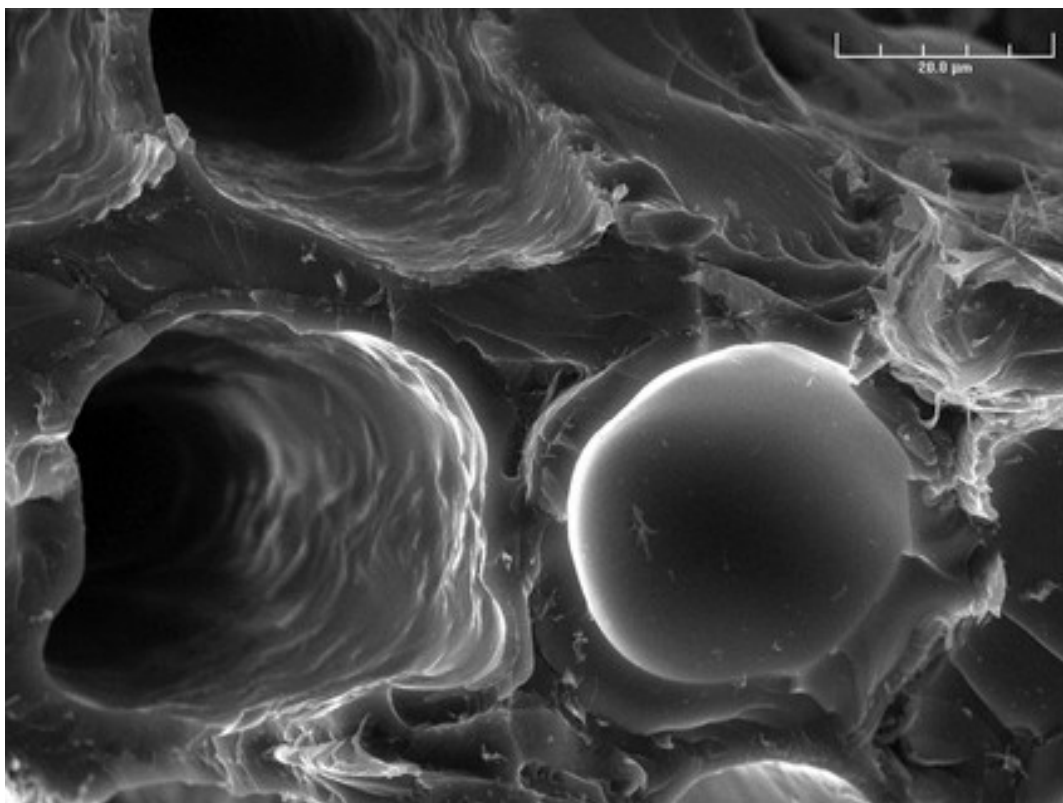


Figure 62. SEM micrograph of pine sample (PS6). The micrograph was taken after being re-conserved with Dr. Smith's MTMS procedure. Two vessels of the cellular wood structure are shown; the one on the right is completely filled with polymer, and the one on the left is coated just by the essential polymer. Note the thinness of the silicone polymer coating.

If alkoxysilanes are applied correctly, the presence of polymer is so minimal that it allows analysis and identification of the morphological characteristic of the materials that compose the object. In the case of wood, the genus, species, and sub-species can be determined because the structures are conserved, maintaining the lumina free of

polymer. In the same way, in the conservation of textile or fabrics, fibers can be identified with the assistance of microscopic analysis.

Despite the interesting results that the use of alkoxysilanes offers, some significant drawbacks derived from this treatment should be addressed. The fact that the procedure acts at a molecular level, creating chemical bonds, means the use of alkoxysilanes modifies the wood's chemical composition, and more important, is irreversible.

As explained earlier, minimal intervention and reversibility are two of the four ethical principles strongly recommended for any conservation procedure for waterlogged wood (Grattan and Clarke 1987:164). Reversibility in conservation is an ethical principle widely accepted and included in the code of ethics of the International Institute for Conservation (IIC-AG 1968). It is a topic that, yet accepted, is debated because of needs from a specific clarification and distinctions (Hellwing 1981:25-27; Horie 1982, 1987:6-10).

If not before, reversibility was first mentioned in the 1840s by restorers in Berlin (Horie 1987:7). It was presented as a necessary ethical principle in Article 8 of the famous Italian document, *Carta Italiana del Restauro* of 1972 (Brandi 1977:129). The article states that any conservation procedure must be required to use techniques and materials that allow future conservation interventions; that is, reversible materials.

However, despite common acceptance of this ethical principle, there are some instances that the ethical principle of reversibility could be made secondary for the sake of other needs or requirements. C.V Horie (1982) stated: "*There are many treatments*

*which are not reversible but which must be accepted as useful and necessary because no better solutions to the problems have been devised, for instance cross-linking polymers are used at present in the conservation of stone*". A perfect example of this principle is represented by the sails of the *Vasa*. The extremely fragile and highly degraded fabrics of the sails of the *Vasa* were meticulously and painstakingly consolidated with thermosetting copolymers of styrene (i.e., 2-ethylhexyl acrylate and isobutyl acrylate). In order to keep the original shape of the sails, they were mounted over a support of fiberglass that had the same light refractive index of the used epoxy resin (Barkman 1967:23; Bengrsson 1975). Needless to say, neither the polymer used nor fiberglass is a reversible material. Yet at the time of the conservation of the sails, no better solution to the problem had been devised; hence the validity of the treatment is unquestionable.

The use of alkoxy silanes for the conservation of stone and other lithic materials provides another example. As explained in Chapter II of this thesis, the use of alkoxy silanes for the conservation of stone and other lithic materials has been in use since the nineteenth century. In the conservation of stone, alkoxy silanes are widely used and accepted by the conservation community, and the ethical principle of reversibility seems not to be a consideration. The advantages of using alkoxy silanes can, in some instances, displace the ethical principle of reversibility to a secondary concern.

There are two main reasons why conservators of stone materials are not stopped by the lack of reversibility when using alkoxy silanes. The first reason is that alkoxy silanes are very similar in composition to the material aimed to consolidate: stone.

Both alkoxysilanes and stone have silicon in their respective compositions. Hence they create a homogeneous union. The second reason lays in the strength of the consolidant. In the search for a good consolidant, conservators of stone look for the restitution of structural strength. Hence, consolidants with strong adhesive properties are desired. In general, the more reversible a material is, the weaker its adhesive properties. Therefore, highly soluble (hence reversible) acrylic resins such as Paraloid® B72 are not preferred for the conservation of stone. On the contrary, alkoxysilanes are preferred as a consolidant that has extremely good adherent properties despite its lack of reversibility (Wheeler 2005).

Those nonreversible consolidants are also desired due to their long-lasting characteristics and estimated service life. How long alkoxysilanes are expected to last in a material depends on many different and complex factors. The longevity of silicone sealants is well known by the polymer industry. This longevity is primarily due to the stability of the basic silicon polymer. The high bond energy of the Si-O bond (108 Kcal/mol) compared to the bond energy of the C-C bond (83 Kcal/mol) of organic materials allows silicone sealants to have higher thermal stability than organic sealants (Grant 1996:10:7705). Although not quoting any data, Dr. Wayne Smith suggested that tests carried out by silicone and polymer industries estimate a 200- to 250-year-long longevity for the silicone polymers (Smith 1997:1:2; 1998:162). Other sources provide more specific data for the estimated service life of silicone rubber. Stark et al. (1982:342-345) quote data showing silicone rubbers have a service life of 15,000 hours at 150 °C, and survive even at 316 °C for 100 hours. In addition, Caprino and Macander

(1987:376) show an estimated service life of silicone rubber of 40 years at 90 °C, two to five years at 150 °C, and two weeks at 316 °C.

For the specific longevity of alkoxysilanes applied to archaeological materials, Dr. Wayne Smith conducted an accelerated ageing test of polymer durability on archaeological materials conserved with silicone oils, with the aid of the accelerated weathering machine Atlas UV 2000. This experiment suggested that after four months of accelerated weathering, subjecting the samples to sharp variations of humidity and temperature, the silicone oil-treated samples were comparable to other samples that had not undergone accelerated weathering (Smith 2003:89). Although this test does not provide detailed quantitative results, it does provide a qualitative evaluation. Another point of reference is that the first artifacts conserved by Dr. Smith at TAMU in 1997 currently present no degradation or discoloration at the macroscopic level, after being on display for 13 years without the aid of any climatic or environmental preventive measures. Finally, in the conference ICOM-WOAM 2010 a rigorous assessment of the condition of an elephant tusk conserved with silicone oil in 1998 has shown that after 12 years the tusk is stable and presents no significant deterioration (Godfrey et al. 2010). In addition to these experiments, the use of alkoxysilanes in the conservation of stone has proven to last long enough (i.e., at least 20 years) in harsh outdoor environmental conditions to validate their widely accepted use (Wheeler 2005:89-108).

Another factor to take into consideration is that, due the extreme thinness of the film form over the conserved object, alkoxysilanes can be reapplied in the future, hence expanding the time expectancy of the treatment. This is also one of the reasons they are



employed in the conservation of stone, in which reapplication is encouraged as maintenance procedure (Oztiirk 1992:42).

Studies have shown that despite the type of consolidant used (and its theoretical reversibility), no treatment is reversible at the molecular level (Horie 1982:3.2). Therefore, the definition of “reversibility” is complex and largely depends on which type of procedure is referred to (i.e., cleaning, consolidation, reassembly, etc.). It has been proposed that it will be more accurate to classify treatments in degrees of reversibility (Jedrzejewska 1981:27-32; Horie 1987:7; Appelbaum 1987:65-73). More particularly, when referring to consolidants, Appelbaum (1987:65-73; 2007:359) proposed the term re-treatability. The notion of re-treatability is one that is often more helpful in evaluating treatments than the idea of reversibility itself (Appelbaum 1987:65-73). While reversibility in consolidation using polymers is clearly not a realistic achievable aim, the desirability of re-treating it at some point in the future remains a desirable goal (Caple 2000:64) As explained earlier, due to the extreme thinness of the film formed over the conserved object, alkoxy silanes can be re-applied in the future; hence, its reapplicability (i.e., re-treatability exclusively with silanes) is high, thus expanding the time expectancy of the treatment and, consequently, expanding the life span of the treated object.

Despite the lack of reversibility, the use of alkoxy silanes brings some positive outcomes. The presence of the polymer is so minimal that it allows analyzing and identifying morphological characteristic of the materials that compose the object. In the case of wood, the genus, species, and sub-species can be determined because the structures are conserved, maintaining the lumina free of polymer. At best, it is possible

to observe structural details as small as the vessels of the longitudinal tracheids that compose the wood. In the same way, in textiles conserved with alkoxy silanes, fibers can be identified with the assistance of microscopic analysis.

Another important advantage to note is the fact that objects conserved with alkoxy silanes acquire the preventive characteristics of the silicone polymer. Although the Si-O bond is susceptible to hydrolysis under extreme pH conditions, it is resistant to most forms of environmental attack. In particular, resistance to oxidation is excellent. Alkoxy silanes are also highly resistant to ultraviolet radiation due to the absence of ultraviolet chromophores in its formulation (Grant 1996:10:7705). Objects or materials coated with alkoxy silanes acquire the polymer characteristics: The object becomes highly resistant to changes in temperature, chemical attacks from acid or bases, and ultraviolet radiation, and also turn into a hydrophobic material; therefore, these objects or materials are less affected by changes in environmental conditions (Wheeler 2005). In fact, recently, alkoxy silanes have been proposed as an effective surface coating to prevent mold or fungal growth on wood (Tshabalala et al. 2009:135-147). These newly acquired characteristics are important to consider when the conserved artifacts are going to be exposed to the public because preventive conservation measures, during shipping or on display, can drastically be reduced.

Finally, the use of alkoxy silanes does not require expensive equipment beyond the normal conservation laboratory tools; this is an advantage in comparison with the expensive requirements of other conservation procedures for waterlogged wood (e.g., heatable conservation tanks, freeze-dryer unit, etc.). Alkoxy silanes are relatively

expensive chemicals. However, alkoxy silanes could be highly efficient consolidants due to two factors: The amount of polymer retained by the treated object is minimal, and the free-flowing polymer can be re-used with a similar material. With re-use of the polymer, the number of artifacts conserved by a given volume of polymer is very high when compared with other consolidants. Hence, despite the expensive price of the chemicals, alkoxy silanes can be considered inexpensive in the long term. As in the case of solvent dehydration procedure, the toxicity and fire hazard related to the solvents should be factors to acknowledge and take into consideration.

## CHAPTER X

### CONCLUSIONS

In this study the feasibility of re-conserving small wood artifacts, previously conserved by total impregnation with PEG, with alkoxysilanes has been tested. Three different wood samples from the *Vasa* Museum Collection have been re-conserved with three different procedures involving alkoxysilanes. The three proposed procedures were: (1) the method used by the Conservation Research Laboratory (CRL) using silicone oil and a crosslinker; (2) a MTMS treatment developed by Dr. Wayne Smith; and (3) a MTMS treatment variation developed by the author.

For the re-conservation of wood previously conserved by total impregnation with PEG, the study demonstrated that the best way to remove PEG from an object is by reverse osmosis in aqueous solution at 60 °C. In this particular instance, Dr. Smith's MTMS re-treatment method has been showed to be less effective in removing PEG from the samples than the use of heated deionized water.

The study has shown that after re-conservation the color acquired by the samples was considered good in all but one of the final samples. From all three re-conservation procedures, the resulting samples show minimal shrinkage on the longitudinal, radial, and tangential axis in the average ratios expected, going from swollen wood to dry wood. The results also demonstrated that, in some cases, it is possible to acquire values in weight and specific gravity very close to those seen in dry wood.

The study showed that results vary depending on the selection of a different viscosity alkoxy silanes (i.e., silicone oil *versus* MTMS). Better results are obtained with lower viscosity alkoxy silanes (i.e., MTMS). As in other consolidation techniques, the selection of a specific consolidant has to be *ad hoc* for each artifact or groups of artifacts. This selection will be largely based on the nature of the artifact, porosity of the material, and degree of preservation, among other factors.

Microscopic analysis of the samples demonstrated that the amount of polymer retained in the samples is minimal. Micrographs have shown that, in the best cases, the thickness of the protective polymer film is in the scale of micrometers, yet is enough to support and confer mechanical strength to the conserved wood structure. Hence, the re-conserved samples acquire physical characteristics very close to those of natural wood. All resulting samples showed minimal shrinkage on the longitudinal, radial, and tangential axis within the average ratios expected going from swollen to dry wood. The results also demonstrated that, in the case of the alternative MTMS re-treatment method, it is possible to acquire values in weight and specific gravity very close to those seen in dry wood. The presence of the polymer is so minimal that it allows analyzing and identifying diagnostic morphological characteristic of the materials.

The study demonstrated that better results are obtained when lower molecular weight polymers are use as consolidants. In these re-conserved pine samples, the use of MTMS (1 cSt), following the procedure proposed by the author in this thesis, has demonstrated to offer better results than the use of silicone oil Dow Corning SFD-1 (~75 cSt). It is logical to assume that the use of silicone oil with a lower molecular weight

than Dow Corning SFD1 will offer better results for the same type and nature of samples.

The results obtained with the use of alkoxysilanes for the re-conservation of previously PEG-impregnated artifacts are very desirable but not reversible. However, it has been explained that in some instances reversibility is not necessarily a drawback. In the consolidation of a material, where the main aim is to confer mechanical and structural strength to the artifact, reversibility is not necessarily a required characteristic. In these cases, re-treatability is an equally desirable and acceptable quality. If the application of alkoxysilanes as consolidant is performed properly, the amount of polymer retained by the artifact is minimal, and hence, the technique is highly re-treatable.

The life span or durability of the alkoxysilanes is a point that requires more study. However, the stability of these alkoxysilane polymers is elevated due to the industrial formulation of the polymers. Therefore, the life span of small wooden artifacts previously conserved by impregnation with PEG could be significantly extended by their re-conservation with alkoxysilanes. Nevertheless, further detailed studies about the stability of archaeological wood conserved with alkoxysilanes should be conducted. Undoubtedly, if these studies would be conducted, they certainly will provide valuable complementary information to this study.

Another advantage of the use of alkoxysilanes is the few basic installations and technical knowledge necessary to conduct this technique. Conservators do not always work for museums or research institutions with advance technology and resources.

Furthermore, heritage often comes from remote places with limited access to technology. Hence, a technique that requires minimal installations and technical knowledge is of great value for the field of conservation. In practical terms, in the world of conservation, sometimes the best technique is not achievable or realistic; therefore, it becomes the enemy of the better techniques.

Wherler (2005:114) in his *Alkoxysilanes and the Consolidation of Stone* describes the duality between theory and practicality in his final thoughts where he states, “*Consolidation of stone with alkoxysilanes, like all conservation treatments, involves elements of the cognitive, the intuitive, and the sensory. Scientists tend to favor the cognitive –the so called objective from knowing- over the more subjective but equally important intuitive and sensory forms of knowing that make up so much of the world of the conservator. Our goal should be a dynamic fusion of these ways of knowing and not their separation. The reward will be better conservation of our heritage*”.

To summarize, this study demonstrated that the re-conservation of small, wood artifacts previously conserved by total impregnation with PEG with alkoxysilanes is not only a feasible approach but also offers quite significant results. The re-conserved samples acquire very close physical characteristics to those of natural wood, and obtain new added properties from the alkoxysilanes that reduce the use of preventive conservation measures during display or storage.

Based on the results of the three re-conservation procedures tested in this study, the author’s proposed alternative MTMS procedure is the most suitable re-conservation method for small wooden objects previously conserved by impregnation with PEG.

Nevertheless, and despite the significant results, the final responsibility in evaluating the pros and cons of using alkoxy silanes for the conservation or re-treatment of waterlogged archaeological wood lies with museum conservators and curators. They should study each particular case as a *unicum*, thoughtfully and in detail, taking into consideration the advantages and drawbacks of alkoxy silanes before applying this procedure.



## GLOSSARY

<b>Anaerobic</b>	Refers to a technical word which literally means <i>without air</i> (where "air" is generally used to mean oxygen).
<b>Capillarity</b>	Is a physical phenomenon where liquid spontaneously rises in a narrow space such as a thin tube, or in porous materials.
<b>Catalysis</b>	The process in which the pace of a chemical reaction is increased by means of a chemical substance known as a catalyst.
<b>Catalysts</b>	A substance, usually used in small amounts relative to the reactants that modifies and increases the rate of a reaction without being consumed or affected in the process.
<b>Chromophore</b>	Is the part of a molecule responsible for its color.
<b>Cross-Link</b>	Are bonds that link one polymer chain to another. They can be covalent bonds or ionic bonds. Term used in the synthetic polymer science field, which usually refers to the use of cross-links to promote a difference in the polymers' physical properties.
<b>Cross-Linking</b>	Is the process in which large polymer molecules react with each other to form a 3-dimensional network.
<b>Covalent Bond</b>	Form of chemical bonding that is characterized by the <i>sharing</i> of pairs of electrons between atoms.
<b>Curing</b>	Is a term in polymer chemistry and process engineering that refers to the toughening or hardening of a polymer material by cross-

linking of polymer chains, brought about by chemical additives, ultraviolet radiation, electron beam or heat.

- Curing Agent** Chemical reagent which creates bonds that link one polymer chain to another, promoting a change in the polymers' physical properties.
- Dehydration** The removal of water from an object.
- Defatting** The removal of fatty acids from an object or tissue lipids.
- Deionized Water** Water from any source that is physically processed to remove impurities.
- EDMA** Ethylenediiminobis (2hydroxy-4methyl-phenil) acetic acid.  
Chelating agent used to the extraction of iron compound for the *Vasa* wood.
- EDS** Electron Dispersion Spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample.
- Elastomers** Term derived from *elastic polymer* often used interchangeably with the term rubber, and is preferred when referring to vulcanisates.
- Fixation** Is a chemical process by which biological tissues are preserved from decay. In the *plastination* technique is used to enhance color preservation.

- Hydrophilic** From Ancient Greek *ὕδωρ (hydor)*, “water” and *φιλία (philia)* “friendship,” refers to a physical property of a molecule that can transiently bond with water through hydrogen bonding.
- Hydrophobic** From Ancient Greek *ὕδωρ (hydor)*, “water” and *Φόβος (phobos)* “fear,” refers to the physical property of a molecule (known as a hydrophobe) that is repelled from a mass of water.
- Homolytic Cleavage** The splitting or dissociation of chemical bonds generating two radicals.
- Heterolytic Cleavage** The splitting or dissociation of covalent bonds generating a cation and an anion.
- Hydrolysis** Is a chemical reaction during which molecules of water ( $\text{H}_2\text{O}$ ) are split into hydrogen cations ( $\text{H}^+$ , conventionally referred to as protons) and hydroxide anions ( $\text{OH}^-$ ) in the process of a chemical mechanism).
- Intonaco** Italian term for the final, very thin layer of plaster on which a fresco wall painting is painted.
- Lithic Materials** Refers to materials pertaining to or consisting of stone.
- Molecular Weight** Is the ratio of the mass of one molecule of a substance to 1/12 of the mass of carbon-12. It is a dimensionless number.
- MTMS** Methyltrimethoxysilane  $(\text{CH}_3\text{O})_3\text{SiCH}_3$  -MTMS-. Hidrolizable multifunctional alkoxyasilane polymer.

**Organoleptic**

**Analysis** Relating to the senses (taste, sight, smell, touch) refers to a inspection perceived by a sense organ.

**Osmosis** It is a physical process in which a solvent moves, without input of energy, across a semi-permeable membrane (permeable to the solvent, but not the solute) separating two solutions of different concentrations.

**Raman-FTIR** Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. Fourier transform infrared (FTIR) spectroscopy is a measurement technique for collecting infrared spectra.

**Silica** The chemical compound silicon dioxide, also known as silica (from the Latin *silex*), is an oxide of silicon with a chemical formula of  $\text{SiO}_2$  and has been known for its hardness since antiquity. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. Silica is the most abundant mineral in the Earth's crust

**Silicones** Are inert, synthetic compounds with a wide variety of forms and uses. Typically heat-resistant and rubber-like. Silicones are polymers that include silicon together with carbon, hydrogen, oxygen, and sometimes other chemical elements.

<b>Silicone Oils</b>	Polymerized siloxanes are not silicone but rather silicon analogues of carbon based organic compounds, and can form (relatively) long and complex molecules based on silicon rather than carbon.
<b>Siloxanes</b>	Are chemical compounds composed of units of the form $R_2SiO$ , where R is a hydrogen atom or a hydrocarbon group. They belong to the wider class of organosilicon compounds. Siloxanes can have branched or unbranched backbones consisting of alternating silicon and oxygen atoms $-Si-O-Si-O-$ , with side chains R attached to the silicon atoms.
<b>Solvent</b>	Is a liquid, solid, or gas that dissolves another solid, liquid, or gaseous solute, resulting in a solution that is soluble in a certain volume of solvent at a specified temperature. The most common solvent in everyday life is water.
<b>Sublimation</b>	Is the transition of a substance from the solid phase to the gas phase without passing through an intermediate liquid phase.
<b>Thermosetting</b>	Plastic or polymer material that irreversibly cures.
<b>Vapor Pressure</b>	Or equilibrium vapor pressure is the pressure of a vapor in thermodynamic equilibrium with its condensed phases in a closed system. All liquids and solids have a tendency to evaporate into a gaseous form, and all gases have a tendency to condense back to their liquid or solid form.

- Viscosity** Is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. In everyday terms (and for fluids only), viscosity is "thickness" or "internal friction".
- XPS** X-ray photoelectron spectroscopy is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material.

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## APPENDIX

Table 13. Measurements of oak waterlogged sample and its sub-samples before and after the different re-conservation treatments applied.

Sample #	Description / Comments	Measurements L.xR.xT <sup>1</sup>	Weight	Volume	Specific Gravity	Color <sup>2</sup>
Waterlogged Sample Vasa # 65486 Find # 24248	Untreated waterlogged oak.	121 x 63 x 25 mm	122.11 g	107.044 cm <sup>3</sup>	1.14 g/cm <sup>3</sup>	Waterlogged exterior: 10YR 3/2 Waterlogged interior (cross-section): 10YR 2/1
WS1	Sub-sample for pre-treatment analysis	Before subdivided: 39 x 24.6 x 30 mm	Waterlogged: 17.3 g	N/A	Same as WS	Same as WS
WS1 sections for pretreatment analysis	WS1a	After Freeze Dry: 38 x 7.5 x 29 mm	Dry: 3.2 g	N/A	N/A	Dry exterior: 10YR 5/3 Dry interior: 7.5YR N4
	WS1b	After Freeze Dry: 38 x 8 x 29 mm	Dry: 3.6 g	N/A	N/A	Dry interior: 7.5YR N4
	WS1c	After Freeze Dry: 38 x 5.5 x 29 mm	Dry: 2 g	N/A	N/A	Same as WS1a
WS2	Sub-sample kept as control of the waterlogged wood	28 x 16 x 30 mm	Waterlogged: 17.3 g	N/A	Same as WS	Same as WS
WS3	Sub-sample kept as control of the waterlogged wood	54 x 20 x 30 mm	Waterlogged: 15.7 g	N/A	Same as WS	Same as WS
WS4	Sub-sample re-conserved with silicone oil	Before re-conservation: 118 x 24.6 x 32.6 mm	Before Waterlogged: 54.1 g	Before Waterlogged: 48.829 cm <sup>3</sup>	Before Waterlogged: 1.10 g/cm <sup>3</sup>	Dry exterior: 10YR 2/1; 10YR 4/3; 10YR 5/4
		After re-conservation: 117.6 x 23.5 x 30.6 mm	After Dry: 34.7 g	After Dry: 47.853 cm <sup>3</sup>	After Dry: 0.72 g/cm <sup>3</sup>	Dry interior: 10YR 2/1; 10YR 3/1; 10YR 4/1
WS4.a	Sub-sample for post-treatment analysis	12.1 x 23.5 x 30.6 mm	After Dry: 4.8 g	N/A	N/A	Same as WS4

<sup>1</sup> Longitudinal x Radial x Tangential lengths.<sup>2</sup> Munsell® soil color chart reference.

Table 14. Measurements of pine EDMA sample and its sub-samples before and after the different re-conservation treatments applied.

Sample #	Description / Comments	Measurements	Weight	Volume	Specific Gravity	Color
EDMA Sample Vasa # 65487. Find # 17396.	PEG extracted and EDMA treated waterlogged pine.	108 x 34 x 100 mm	Waterlogged: 356.60 g	316.910 cm <sup>3</sup>	1.12 g/cm <sup>3</sup>	Waterlogged exterior: 10YR 3/6 Waterlogged interior: 10YR 7/4; 10YR 4/6
ES1	Sub-sample for pre-treatment analysis	Before subdivided: 52.6 x 33.8 x 27.5mm	Waterlogged: 69.8 g	N/A	Same as ES	Same as ES
ES1 sections for pretreatment analysis	ES1a	After Freeze Dry: 52 x 10.5 x 25 mm	Dry: 5.9 g	N/A	N/A	Dry exterior: 10YR 7/4 Dry interior: 10YR 8/3
	ES1b	After Freeze Dry: 52 x 10 x 25 mm	Dry: 5.4 g	N/A	N/A	Dry interior: 10YR 8/3
	ES1c	After Freeze Dry: 52 x 10.5 x 25 mm	Dry: 5.9 g	N/A	N/A	Dry exterior: 10YR 7/4 Dry interior: 10YR 8/3
ES2	Sub-sample kept as control of the EDMA treatment	52.6 x 33.8 x 35 mm	Waterlogged: 69.7 g	N/A	Same as ES	Same as ES
ES3	Sub-sample re-conserved with author's MTMS	Before re-conservation: 52.6 x 33.8 x 36.9 mm	Before Waterlogged: 49.3 g	Before Waterlogged: 44.385 cm <sup>3</sup>	Before Waterlogged: 1.11 g/cm <sup>3</sup>	Dry exterior: 10YR 8/4; 10YR 6/6 Dry interior: 10YR 7/3 Interior Resin: 10YR 4/4
		After re-conservation: 52.3 x 33.6 x 36.8 mm	After Dry: 20.9 g	After Dry: 44.169cm <sup>3</sup>	After Dry: 0.47 g/cm <sup>3</sup>	
ES3.a	Sub-sample for post-treatment analysis	8 x 33.6 x 36.8 mm	Dry: 2.8 g	N/A	N/A	Same as ES3
ES4	Sub-sample re-conserved with silicone oil	Before re-conservation: 55.7 x 34.1 x 101.8 mm	Before Waterlogged: 174.7g	Before Waterlogged: 166.758 cm <sup>3</sup>	Before Waterlogged: 1.04 g/cm <sup>3</sup>	Dry exterior: 10YR 8/4; 10YR 7/4; 10YR 6/6; 10YR 4/6 Dry interior: 10YR 8/4; 10YR 3/2 Interior Resin: 10YR 3/3
		After re-conservation: 54.6 x 33.2 x 98.7 mm	After Dry: 130.8g	After Dry: 162.319 cm <sup>3</sup>	After Dry: 0.80 g/cm <sup>3</sup>	
ES4.a	Sub-sample for post-treatment analysis	21 x 33 x 21 mm	Dry: 10.2 g	N/A	N/A	Same as ES4



Table 15. Measurements of pine PEG sample and its sub-samples before and after the different re-conservation treatments applied.

Sample #	Description / Comments	Measurements	Weight	Volume	Specific Gravity	Color
PEG Sample Vasa # 65485 Find # 13473	PEG treated pine.	170 x 82 x 31 mm	292.92 g (302.92 g with Ref.# plate)	333.508 cm <sup>3</sup>	0.87 g/cm <sup>3</sup>	Dry exterior: 5Y 2.5/1; 5Y 2.5/2 Sulfur spot: 5Y 4/4 Dry interior: 2.5Y 4/2; 10YR 4/2
PS1	Sub-sample for pre-treatment analysis	Before subdivided: 45 x 37.5 x 33 mm	43.1 g	48.130 cm <sup>3</sup>	0.89 g/cm <sup>3</sup>	Same as PS
PS1 sections for pretreatment analysis	PS1a	45 x 37.5 x 10.5 mm	15.2 g	N/A	N/A	Dry exterior: 5Y 2.5/1; 5Y 2.5/2 Dry interior: 2.5Y 4/2; 10YR 4/2
	PS1b	45 x 37.5 x 10 mm	13.3 g	N/A	N/A	Dry interior: 2.5Y 4/2; 10YR 4/2
	PS1c	45 x 37.5 x 11 mm	14.6 g	N/A	N/A	Dry exterior: 5Y 2.5/1; 5Y 2.5/2 Dry interior: 2.5Y 4/2; 10YR 4/2
PS2	Sub-sample kept as control of the original PEG treatment	38 x 37.5 x 33 mm	36.5 g	41.715 cm <sup>3</sup>	0.87 g/cm <sup>3</sup>	Same as PS
PS3+PS4+PS5		165 x 43.7 x 33 mm	150.7 g	177.54 cm <sup>3</sup>	0.84 g/cm <sup>3</sup>	Same as PS
PS3	Sub-sample kept as control of the PEG extraction	Waterlogged: 26 x 43 x 33 mm	Waterlogged: 57.2 g	Waterlogged: 34.572 cm <sup>3</sup>	Waterlogged: 1.65 g/cm <sup>3</sup>	N/A
PS4	Sub-sample re-conserved with author's MTMS	Before re-conservation: 34.3 x 43.7 x 33.6 mm	Before re-conservation Dry: 36.6 g	Before re-conservation: 42.139 cm <sup>3</sup>	Before re-conservation: 0.86 g/cm <sup>3</sup>	Dry exterior: 10YR 5/4; 10YR 4/3; 10YR 4/4

Sample #	Description / Comments	Measurements	Weight	Volume	Specific Gravity	Color
		After re-conservation: 34 x 41.4 x 33 mm	After re-conservation Dry: 29.7 g	After re-conservation 40.930 cm <sup>3</sup>	After re-conservation 0.72 g/cm <sup>3</sup>	Dry interior: 10YR 5/4; 10YR 5/6; 10YR 3/3 Interior Resin: 10YR 4/3 Dirty PEG: 10YR 3/1
PS4.a	Sub-sample for post-treatment analysis	9.2 x 41.4 x 33 mm	Dry: 7.9 g	N/A	N/A	Same as PS4
PS5	Sub-sample re-conserved with silicone oil	Before re-conservation: 108 x 43.2 x 34.5 mm	Before re-conservation Dry: 87.6 g	Before re-conservation: 100.793 cm <sup>3</sup>	Before re-conservation: 0.86 g/cm <sup>3</sup>	Dry exterior: 10YR 5/3; 10YR 3/2; 10YR 2/2
		After re-conservation: 107 x 41.6 x 33.6 mm	After re-conservation: Dry: 87.4 g	After re-conservation 98.893 cm <sup>3</sup>	After re-conservation 0.88 g/cm <sup>3</sup>	Dry interior: 10YR 4/4; 10YR 3/2 Waxy PEG: 10YR 2/1
PS5.a	Sub-sample for post-treatment analysis	14.5 x 41.6 x 33.6 mm	Dry: 15.9 g	N/A	N/A	Same as PS5
PS6	Sub-sample re-conserved with Smith's MTMS	Before re-conservation: 85 x 37.5 x 31.9 mm	Before re-conservation Dry: 57.1g	Before re-conservation: 65.298 cm <sup>3</sup>	Before re-conservation: 0.87 g/cm <sup>3</sup>	Dry exterior: 10YR 4/4; 10YR 2/2 Dry interior: 10YR 6/3; 10YR 5/3 Cross-section: Int 10YR 4/2 Ext 10YR 3/3 + white crystals Interior Resin: 10YR 4/3 Dirty PEG + white crystals: 10YR 3/1
		After re-conservation: 84.7 x 36.5 x 30.2 mm	After re-conservation Dry: 63.8 g	After re-conservation 64.029 cm <sup>3</sup>	After re-conservation 0.99 g/cm <sup>3</sup>	
PS6.a	Sub-sample for post-treatment analysis	11.5 x 36.5 x 30.2 mm	Dry: 10.6 g	N/A	N/A	Same as PS6

## VITA

Carlos Cabrera Tejedor received his first Bachelor of Arts degree in Applied Arts to Art Restoration (specialty in Painting) from the Center for Studies in Art Restoration at Madrid in 2000. He also received a second Bachelor of Arts degree in Conservation and Restoration of Cultural Goods (specialty in Archeology) from the School of Conservation and Restoration of Cultural Goods at Madrid in 2003. He entered the Nautical Archaeology Program at Texas A&M University in September 2006 and received his Master of Arts degree in December 2010. His research interests include conservation and restoration, underwater and marine archaeology, history of seafaring and the history of the ancient world. He has worked in underwater excavations and surveys throughout the Mediterranean and the Atlantic Oceans. He has received a number of scholarships and fellowships in support of his studies from institutions including the Spanish Ministry of Culture, and the Marian M. Cook fellowship of Institute of Nautical Archaeology. The results of his research projects have been published in journals, book chapters, and presented at several international conferences.

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