## CHARRED WOOD CONSOLIDATED WITH THERMOPLASTIC RESINS

Abstract: Charred wood objects can retain important information about the object's original form, including clearly discernable carved surfaces. Nonetheless very little research has been conducted into the consolidation of charred wooden objects. This research is a preliminary investigation of the use of a thermoplastic resin as a consolidant for charred wood objects. Specimen sets were prepared from four woods: ash, maple, cherry and oak. Specimens were carbonized in a controlled environment, in the absence of oxygen. The consolidant used was a 10% solution of Butvar B-98 in a mixture of 60/40 mixture of ethanol and toluene. Sixty percent of each specimen set was consolidated by immersion in the consolidant under vacuum. A gloss meter was used to measure changes in the surface appearance of the consolidated char. Sections from consolidated specimens were examined by scanning electron microscope to determine the penetration of the consolidant into the charred specimen. Consolidated and unconsolidated specimens were exposed to elevated relative humidity. The response of the consolidated and unconsolidated specimens was compared by noting changes in the dimensions and masses of the specimens.

## INTRODUCTION

When wood is subjected to prolonged heat in an oxygen-starved atmosphere, wood char is formed. Because wood char is created due to the absence of oxygen, it undergoes very different chemical processes than those that occur as a result of combustion. Charred wood is often recovered from archaeological excavations because it is chemically stable and no longer has organic constituents that biological organisms might consume. However, due to its extremely fragile nature, it seldom survives intact. (Mols 1999, 7).

Charred wooden objects can retain important diagnostic, cultural and technological information concerning the original object, which would have been lost had oxygen been

present. The following image of a charred wooden cradle is an example of the level of detail that can survive in wood char in an archaeological site. The salient information is still clearly visible. The wealth of detail that can be retained within, and extracted from charred wood, along with the surprising endurance of carbonized objects in archaeological sites makes the conservation of charred wooden objects an important objective for conservators in research and practice.



Figure 1: Charred wooden cradle recovered from the archaeological site of Herculaneum, Italy. (Photo: Krysia Spirydowicz)

My interest in charred wooden objects began while working as a student intern on the Gordion Furniture Project, in Turkey, under the supervision of Krysia Spirydowicz. Gordion is the capital of the ancient Phrygian Empire, once ruled by the famous 8th century BC King Midas, and was in existence from the 9th to 2nd century BC. The site consists of two parts, a royal cemetery containing burial mounds, similar to King Midas's burial mound, and a city mound, which contains a number of occupation levels (Young 1981).



Figure 2: Tumulus MM (Tomb of King Midas) Gordion, Turkey. (Photo: Kim Cullen Cobb)



Figure 3: Excavation at 8<sup>th</sup> century BC city mound. (Photo: Kim Cullen Cobb)

Excavations at Gordion have been directed by the University of Pennsylvania since 1950 (Young, 1981). The furniture and wooden objects from the excavations, including King Midas's tomb and the City Mound, now reside at the Museum of Anatolian Civilizations in Ankara, Turkey. They are all part of the Gordion Furniture Project (Spirydowicz



1996). Included within this collection are carbonized wooden fragments, which are the remains of an ancient fire, excavated from the destruction level of the City Mound, at Gordion (Young 1981). During my internship I had the opportunity to study and photograph some of these charred objects.

Figure 18: Charred, carved wooden bowl from the City Mound, Gordion. (Photo: Kim Cullen Cobb)

No effective method of preserving carbonized wood had been developed prior to the 1900s, consequently charred wooden objects excavated before this time, from archaeological sites such as Herculaneum, have subsequently disintegrated (Mols 1999, 25). There have been various explanations of the manner in which Herculaneum was covered (De Carolis and Patricelli 2003; Deiss 1985; Mols 1999). The current view is that Herculaneum was flooded by a hot flow of liquid lava from the eruption of Mount

Vesuvius in AD 79. Analysis of the charred wood at Herculaneum, such as this door frame, pictured below, indicates that the wood was charred at temperatures of approximately 400°C, which would be consistent with this type of lava flow. The lava then hardened into a crust under which the town lay hidden for over 16 centuries (De Carolis and Patricelli 2003).



Figure 5: Charred door frame, Herculaneum, Italy. (Photo: Krysia Spirydowicz)

The record of treatment applied to the charred wood at Herculaneum, provides some historical perspective on the conservation of charred wood. The various consolidants used included a solution of mineral oil added to paraffin-wax, a solution of wax and petrol, and a mixture of carbon powder and paraffin-wax. Similar conservation methods were also attempted in the 1950s and 60s on dried archaeological wood, all with poor results. Mols reports the following from the furniture at Herculaneum: "In many cases the protective layer can still be seen on the surface of the furniture as a thick, black crust, obscuring many details such as the structure of the wood, the marks of carpentry tools and the nature of the joints" (Mols 1999, 29).



Figure 6: Detail of wax drip from charred wood beam, Herculaneum. (Photo: Krysia Spirydowicz)

This above image demonstrates some other drawbacks inherent in wax-based consolidants. Highlighted is a string-like piece of wax dripping from a treated structural timber. The wax-based consolidant has softened in the heat and is dripping from the charred wood.

In subsequent years thermoplastic resins such as Paraloid B-72, Butvar B-90 and Butvar B-98, in various polar and non-polar solvents, have emerged as alternatives to wax solutions for consolidating dried archaeological wooden objects. Butvar B-98 has found widespread use as a consolidant in the conservation of dried archaeological and historic wooden artifacts, and has been successfully used for the past 20 years on the dried wooden artifacts from the Gordion Furniture Project (Spirydowicz 1996; Spirydowicz *et al* 2001).

This research attempts to determine if consolidants, which are commonly applied to dried archaeological wood, can be successfully applied to charred wooden objects. The two

consolidants used are a 10% solution of Butvar B-98 in a 60/40 mixture of ethanol and toluene, and a 10% solution of Paraloid B-72 in acetone.

The following is a brief description of the process of charring, in order to demonstrate how the cracking that takes place in charred wood is a direct reflection of differences between the chemistry of charring and the chemistry of combustion.

Wood char from archaeological contexts is created at temperatures between 300 and 1000°C. In theory, the heating of wood to form char takes place in an anaerobic environment, with the loss of water and alcohol. Figure 7, below, is an example of wood that is heated above room temperature; the adsorbed water is driven off and the strength of the wood increases as drying takes place at temperatures below 100°C (Goldstein 1972, 309). Above 100°C chemical bonds begin to break. Dehydration continues to 200°C during which time wood looses about 35 percent of its total weight in the form of vapor, non-combustible gases, and organic compounds. These reactions are endothermic and continue past 200°C. Figure 8 is an example of wood that is heated to between 100°C and 200°C. The most extreme change is longitudinal shrinkage due to the rearrangement of bonds, leading to the catastrophic loss of cellulose. These changes occur between 200°C and 400°C (Beall, Blankenhorn and Moore 1974, 214). Figure 9 is an example of wood that is heated to between 200°C and 400°C.



Figure 7

Figure 8

Figure 9



Figure 10

Figure 11

Figure 12

Cellulose is a highly crystalline material, providing strength and stiffness to wood (Schniewind 1989, 39). The chemical alteration of this material in the carbonization process helps explain why charred wooden artifacts are often light and brittle. Below 300°C thermal decomposition is endothermic and, therefore, dependent on a heating mechanism. Above 300°C, thermal decomposition is driven by exothermic reactions resulting from the breakdown of cellulose and lignin, and the production of flammable gases and tars. These reactions cause the temperature of the wood to rise spontaneously. If oxygen is available, these flammable gasses will combust. In the absence of oxygen flammable gases and tars are released, and the breakdown of cellulose continues with the formation of char (Caple, Murray 1994). Figures 10, 11 and 12 provide a visual example of the progressive decomposition of wood as a result of exothermic reactions taking place within the cellulose structure as it is heated above 300°C in the absence of oxygen. Thermal decomposition continues leading to the partial reorganization of cellulose by 320°C. (Caple, Murray 1994).



Figure 13

Figure 14



Figure 15



Figure 16

Figure 17

Micro- and macro-cracking appear as the consequence of two mechanisms taking place within the char; the first is the pressure created by the release of gases from chemical changes in the cellulose structure and the reduction in

volume as cellulose is chemically altered. The second is differential reaction rates in the cellulose and lignin, which create sheer stress within the char. The cracks that form increase the surface area of the char, making it much more hygroscopic. The accumulation of chemical and physical changes in the wood structure result in a material that is extremely fragile, intolerant of mechanical abrasion, and very responsive to fluctuations in relative humidity (Beall *et al.* 1974; McGinnes *et al*, 1971; Schniewind 1989, 39).

While the process of charring can eventually lead to the complete disintegration of the physical structure in wood, this research is concerned with those artifacts that have charred at temperatures that enable the retention of salient information concerning the original object. Finding alternate methods for consolidation and preservation of charred artifacts, which contain valuable cultural, historical or archaeological information, is the ultimate goal of this research.

The following is an example of the effect of charring on the mass and volume of wood. A kiln-dried, uncharred specimen of maple measured 20.6 mm by 17.8 mm by 17.6 mm, and weighed approximately 4.0 grams. After charring at 330°C the charred sample measured 19.3 mm by 14.3 mm, by 12.8 mm, and weighed 1.51 grams. This represents a 62 percent reduction in mass, and a 45 percent reduction in overall volume. This is the challenge: to successfully consolidate a charred material, which is extremely vulnerable to cracking.

## METHODOLOGY

In basic terms, the work of this research involves charring samples of different woods, consolidating some and leaving others unconsolidated, and then testing the two sets of samples for changes in stability and appearance as a consequence of consolidation. The stability of the two sets of samples were compared by performing compressive strength tests, using an Instron machine, and surface durability tests, using an ASTM Pencil Test.

Three additional observations were made using a scanning electron microscope to determine the extent of penetration of the consolidant into the char; a Glossmeter to measure changes in surface gloss; and visual and microscopic inspection for cracks.

# **EXPERIMENTAL**

The types of wood selected for this research were some of the hardwoods commonly used in furniture making: cherry, ash, oak and maple. Twenty-two cubes of each of these hardwoods were each cut to measure approximately 20 millimeters by 18 millimeters by 18 millimeters, using a table saw. All the samples were weighted and measured before treatment.

Twenty prepared cubes of each of these woods were then charred in a nitrogen environment at 330°C. In each charring run, three wood cubes were placed in the center of the tube in the furnace. A thermocouple, next to the wood cubes, was wired to a programmable controller that regulated the furnace temperature at a more or less constant 330°C for two hours. Air was expelled by pumping nitrogen gas into one end of the charring tube. The nitrogen was bubbled out the opposite end through a beaker of water to visually confirm the flow of the gas and prevent air from coming back into the chamber. After charring, the cubes were weighed and measured. Figure 18, on the following page, is a diagram of the charring furnace.

The benefits of this method of charring are twofold and have to do with exothermic reactions that take place within the wood during charring. Firstly the constant flow of nitrogen gas helps to cool the char when exothermic reactions within the char begin to

take place. Secondly, the thermocouple, which controls the temperature of the furnace next to the charring wood, is also responsive to the heat generated from exothermic reactions taking place within the char. The thermocouple signals the furnace to drop in temperature when the temperature in the charring wood beings to rise spontaneously, thereby maintaining the char temperature at a more or less constant 330°C. The result is a charred sample with a uniform surface devoid of macro-cracks, making it much easier to monitor changes occurring in the char as a result of treatment.



Figure 18: Diagram of tube furnace used for wood charring.

Three consolidation methods were used to treat samples using the Butvar B-98 solution. The first method involved soaking the charred cubes for 24 hours, followed by vacuum impregnation using a tap water aspirator, to create a vacuum of 20 cm Hg for 20 minutes. The second method involved soaking the charred cubes for 24 hours, without vacuum impregnation. And the third method involved soaking the charred cubes for 72 hours without vacuum impregnation. Only one consolidation method was applied using the Paraloid B-72 solution. The method involved soaking the charred samples for 72 hours without vacuum impregnation.

Finally one set of charred samples from each wood type was soaked in a 60/40 mixture of ethanol and toluene without the addition of a consolidant, and another set of charred samples from each wood type was soaked in acetone. The samples were weighed and measured immediately after treatment and then at regular intervals while they were drying.

Initially, samples consolidated with Butvar B-98 were dried in an oven at 45°C for one month in order to encourage the elimination of solvents in the consolidant. When cracks were noted in the drying char a slow drying method was employed for subsequent sample sets, with the expectation that this would reduce the production of cracks in the char during consolidation. Slow drying involved loosely wrapping the consolidated samples in polyethylene, and exposing them to air for a brief period each day over the course of one week. Some charred samples remained untreated so that they could be compared with the consolidated samples.

## RESULTS

The results of this research are as follows: cracking occurred in 11 of the 16 samples soaked for 24 hours in Butvar B-98, then vacuum impregnated and oven dried at 45°C. Cracking occurred in nine of the 12 samples soaked for 24 hours in Butvar B-98 and oven dried at 45°C. Cracks developed in all six samples after soaking for 72 hours in the Butvar B-98 consolidant, combined with slow drying. Cracks developed in five of the six

samples soaked for 72 hours in the Paraloid B-72 consolidant combined with slow drying. Cracking occurred in two of the three samples soaked in a 60/40 mixture of ethanol and toluene. Cracking occurred in all three of the samples soaked in acetone.

Consolidation method	Consolidant or solvent	Total # of chars treated	Total # of chars cracked
Soak 24 hrs. vacuum oven dry	Butvar B-98	16	11
Soak 24 hrs. oven dry	Butvar B-98	12	9
Soak 72 hrs.	Butvar B-98	6	6
Soak 72 hrs.	Paraloid B-72	6	5
Soak 24 hrs.	60/40 EtOH/Toluene	3	2
Soak 24 hrs.	Acetone	3	3

TABLE	1:	Results
		<b>I C O C I C O</b>

Overall 78 percent of the charred samples that received treatment of any type cracked as a result of that treatment. Charred material is highly absorbent. When these charred samples are immersed in solvent or consolidant the increase in mass and volume is significant. Based on these results it is apparent that the absorption of solvents and consolidants in charred wooden samples presents a considerable risk to the structural integrity of charred material.



To illustrate the point, consider one example taken from a charred sample of maple, before and after immersion in Butvar B-98. The initial addition of consolidant caused an increase in mass of 142 percent and a corresponding volumetric increase of 36 percent. The mechanical stresses induced by an initial 36 percent increase in volume are significant. The result of this stress is the visual development of cracks in the treated char.

The graph in Figure 20, below, compares the compressive strength of charred wood consolidated with Butvar B-98, and unconsolidated charred wood. For each wood type, the solid colored bar is the unconsolidated charred material and the hatched bars represent samples consolidated by two different methods. The consolidated material is stronger in every instance. The improvements range from less than three percent to 47 percent. A 47 percent improvement is significant, however, the improvement relates to a



Figure 20: Results

material that is very weak and fragile, so it does not necessarily translate into the capacity to support significant load. Consequently resulting structural gains, which may be significant, may not be large enough to justify the risks of inducing major cracking in the object.

Results from measurements taken on unconsolidated and consolidated char samples using the Glossmeter show an increase in surface gloss as a result of consolidation. The difference in surface texture among the charred samples may have influenced the following results. For example, the readings on charred maple samples consolidated with Paraloid B-72 (outlined in red in Table 2) seem anomalous compared with the others. The general increase in surface gloss, measured by the Glossmeter, is consistent with visual inspection.

	Maple	Ash	Cherry
Unconsolidated	0.9	2.4	3.1
Consolidated with Butvar B-98	1.9	4.5	4.4
Consolidated with Paraloid B-72	1.0	5.4	4.3

Average Glossmeter readings:

# TABLE 2. Results

The film hardness by pencil test clearly indicates that there is a significant increase in the surface durability of the consolidated charred samples compared to unconsolidated charred samples. All of the unconsolidated charred samples tested by this method have a



surface hardness of 8B. Consolidated charred samples show an increase in surface hardness that ranges between HB for the ash samples consolidated with Butvar B-98 and Paraloid B-72, and 2H for the charred maple samples consolidated with Paraloid B-72. These results are outlined in Table 3, above.

Four different consolidated charred specimens were selected for viewing using a scanning electron microscope. Table 4 lists the specimens and the distance from the end grains to the surface viewed. Figure 12 and 13 are images captured through the SEM showing the break surface of a maple specimen (M6), 10mm from the end of the char specimen and an ash specimen (A6), 6mm from the end of the char specimen. Note the tubular and thread-like protrusions of thermoplastic resin extending from the vessel elements within the char. These images indicate that the thermoplastic resin has penetrated deeply within the char specimens.

Specimen viewed using SEM	Location of test (mm from end grain)
M6	10mm
M6	6mm
A6	6mm
A6	3mm
A2	6mm
C2	6mm

TABLE 4. Locations on specimens viewedusing a scanning electron microscope.



Figure 21: SEM at break edge of maple sample (M6) 10mm from end of char specimen. Note tubular and thread-like protrusions of thermoplastic resin (300X magnification).



Figure 22: SEM at break edge of ash (A6) sample 6mm from end of char specimen. Note tubular protrusions of thermoplastic resin (1500X magnification).

## CONCLUSION

This research has not shown any significant difference between Butvar B-98 and Paraloid B-72 as consolidating solutions, however further testing is necessary in order to verify this. Contrary to the results from the first set of observations, accelerated drying does not appear to be any worse at causing cracking than the slower drying methods tried later. Based on these results, it appears that the absorption of solvents and consolidants in charred wooden samples represents a considerable risk to the structural integrity of charred material. This may be the single most important observation that this research has illuminated. All of the methods used put a great deal of consolidant into the samples. Other methods that apply much smaller amounts might yield useful benefits in surface durability without producing the large scale cracking observed in this work. In all regards these results point to the need for further research in this area.

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