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The Effects of Butvar B-98 on Bronze

ABSTRACT

In the early 1990's, planning for the preservation of a composite wood and bronze serving stand at the Gordion Furniture Project in Turkey prompted the testing of a variety of materials to determine the best wood consolidant and coating for the bronze studs on the stand. The preliminary results indicated that Butvar B-98, a poly(vinyl butyral) resin used in conservation as a wood consolidant, could have a corrosive effect on the bronze. Testing was therefore carried out at Queen's University to evaluate the potential corrosivity of Butvar B-98 to bronze. Oddy testing was performed on bronze coupons and bronze studs in the presence of Butvar B-98 cast films. Corrosion of the coupons was determined by weight measurements, visual observations, and XRD analysis. The Butvar B-98 films from the test chambers were also analyzed by Fourier transform infrared spectroscopy (FTIR) and cold extraction of Butvar B-98 films was performed for pH testing. Although further testing is suggested, the results from this study indicate that Butvar B-98 is safe to use in association with bronze and that composite objects, such as the Tumulus W serving stand, should not undergo accelerated corrosion due to previous treatments with Butvar B-98.

1. INTRODUCTION

From 1950 to 1973, excavation at the site of Gordion produced one of the largest and most significant collections of wooden objects to survive from the ancient world (Simpson and Spirydowicz 1999). Many of the wooden artifacts from Gordion, the ancient Phrygian capital in central Anatolia, Turkey (fig.1), are believed to date to the eighth century B.C., a period of wealth and prosperity coinciding with the reign of King Midas. The wooden artifacts, which include furniture, carved figurines, plates, spoons, bowls, and other small objects, are all of extremely fine craftsmanship and much of the furniture is intricately decorated with fine wooden inlay and openwork carving.

The survival of these ancient wooden objects is primarily attributed to the continuous protection offered by the tumuli in which they were buried. These mounds contain tomb structures at their center, which provided relatively stable environmental conditions for over 2500 years (fig.2). Physical damage, however, had occurred to objects in Tumulus W and Tumulus P as the chambers had collapsed at some point in their history due to the weight of the overlying mounds. In addition, water from a drilling rig had entered Tumulus MM during excavation, causing severe water damage in some of the wooden objects.

Figure 1: Map of Anatolia

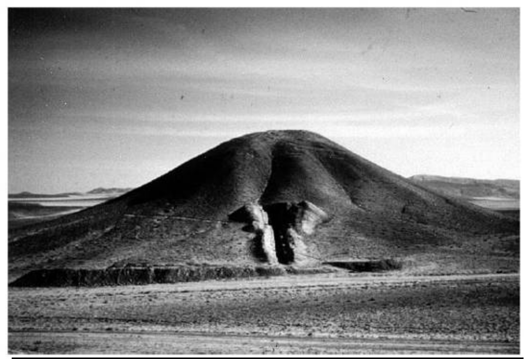

Figure 2: Tumulus MM (Simpson and Spirydowicz 1999)

After excavation, the wooden furniture was transferred to the Museum of Anatolian Civilizations in Ankara for further study and long-term storage. Further examination was conducted at the museum and technical drawings produced soon after the furniture arrived. After this initial activity, however, the furniture remained virtually untouched in museum storage until 1981 when the Gordion Furniture Project was organized by Elizabeth Simpson of the University of Pennsylvania Museum. The main objective of this project was to study and re-publish the wooden furniture, much of which had been incorrectly drawn and identified in the original field notes and drawings. A conservation component, however, was soon found necessary in order to treat the wooden objects which were found to be fragile and largely obscured by grime. Over the next two decades, conservation was carried out seasonally on many of the wooden furniture pieces and small wooden objects.

Cleaning of the darkened wax and Alvar coatings from the furniture surfaces was a relatively straightforward process as these materials were still soluble in common solvents applied by swab or poultice. While significant lightening of the furniture was achieved, in order to strengthen the fragile wood, the pieces required consolidation. The conservator treating the furniture in the early years, Robert Payton, consulted the conservation literature, looking for a material that would satisfy several requirements. The consolidant had to: "Impart strength to the wood so that it could be handled and displayed; cause little to no discoloration of the wood, thereby maintaining the contrast between the boxwood and the dark juniper inlays; maintain, where possible, the structural dimensions of the wood; act as an adhesive for loose inlays and fragments; provide reasonable protection against fluctuating humidity; and be available, with its solvents, in Turkey." (Payton 1984)

Choice of Consolidant

Several studies at the time pointed to the poly(vinyl butyrals) as ideal consolidants for dry wood. A treatment by Bob Barclay at the Canadian Conservation Institute (CCI) had successfully used Butvar to consolidate a large 18^{th} century English fire engine (Barclay 1981). The choice of consolidant in this case, Butvar B-90, was based on extensive research performed at CCI by David Grattan into the properties of several materials used in the consolidation of dry wood. The poly(vinyl butyrals) were found to perform better than the acrylic resins and poly(vinyl acetates) in terms of mechanical strength, flexibility, stability and solubility in non-toxic solvents (Grattan 1980). Virtually no shrinkage or expansion was observed in the wood treated with Butvar, and only minimal color change was found to occur (Grattan 1980; Barclay 1981). Butvar also has very good adhesive properties, a relatively high T_g, and its viscosity can be adjusted depending on the solvent carrier used. The testing and use of Butvar B-98 in conservation has since been reported in numerous reports and publications, confirming these early observations (Wang and Schniewind 1985; Nakhla 1986; Grattan and Barclay 1988; Sakuno and Schniewind 1990; Carlson and Schniewind 1990; Battram 1991;

Schniewind and Eastman 1994; Kres and Lovell 1995; Paterakis 1996; Toutloff 1999; Spirydowicz et al. 2001; Warner 2001)

Importantly for the conservators at the Gordion Furniture Project, Butvar B-98 could be easily imported into Turkey along with its solvents. The mixture of Butvar known as B-98 was chosen specifically for its low molecular weight as the average pore diameter of the boxwood used in much of the furniture is extremely fine, preventing larger molecules from penetrating deep enough into the wood (Payton 1984). Upon testing of different concentrations, it was found that a 5% solution of Butvar Resin in 50/50 ethanol/toluene provided an ideal combination of low viscosity and slow evaporation (Payton 1984). Vacuum impregnation was eventually introduced into the treatment procedure using purpose built chambers and a 10% solution of Butvar B-98 in 60/40 ethanol/toluene (fig.3)(Spirydowicz et al. 2001).

Figure 3: John Childs applying pressure for Consolidation (Simpson and Spirydowicz 1999)

Tumulus W Serving Stand

In 1990 examination and treatment of the Tumulus W serving stand began. Excavated in 1959, the serving stand from Tumulus W had been badly damaged from the collapse of the tomb roof and was therefore in a fragmentary state upon its discovery. Based on the intricate openwork design, the archaeologist in charge of the excavation, Professor Rodney S. Young, had identified the two remaining planks as parts of a screen. Although its original form and function are speculative, based on contextual evidence, these fragments are now believed to be part of a serving stand, several of which were found in the other tumuli at Gordion. The now fragmentary stand is carved in boxwood and covered profusely with small bronze studs (figs.4, 5).

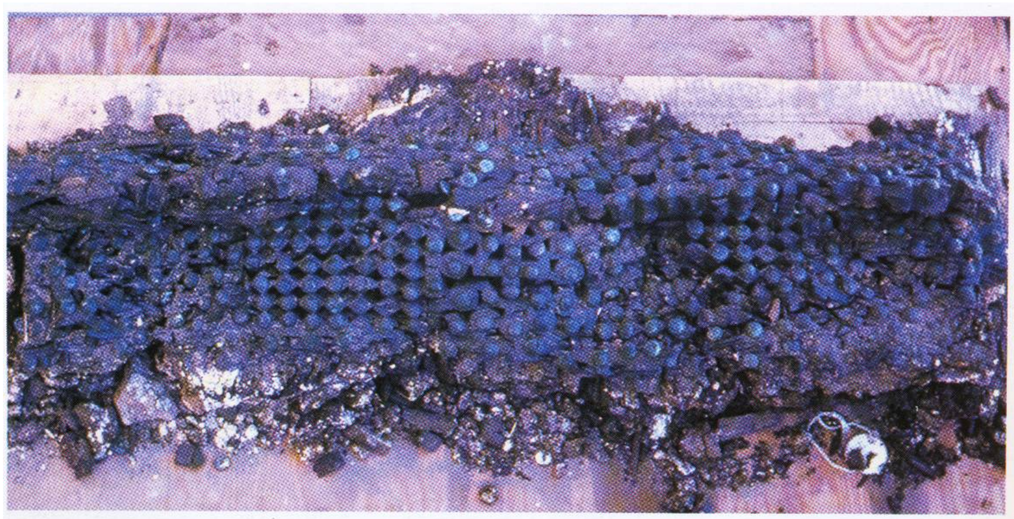

Figure 4: Wooden "screen" from Tumulus W after removal from tomb (Simpson and Spirydowicz 1999)

Figure 5:Tumulus W serving stand after conservation (Simpson and Spirydowicz 1999)

While the carved boxwood was a familiar material for the conservators at the Gordion Furniture Project, the presence of the bronze studs presented a slightly more complex situation. Additional interactions between the conservation materials had to be considered, and preliminary testing to this end was therefore carried out.

In 1991, a student intern at the Gordion Furniture Project carried out the initial testing of materials on a variety of metal coupons. Testing parameters followed a modified ASTM standard for an acetic acid salt spray chamber (ASTM 1983). A series of copper and copper alloy coupons were coated with a variety of consolidants, including Butvar B-98, and exposed to 95% RH in the presence of a salt solution acidified with acetic acid to a pH of 3.5. (Ng 1992). After two weeks it was found that the coupons coated with 10% Butvar B-98 had corroded to a greater extent than the control coupons, which had been left uncoated. Further testing of coatings on the loose studs from the Tumulus W serving stand produced mixed results. Bronze disease developed in most cases on the studs coated with 10% and 30% Butvar B-98; however, the type and amount of corrosion that developed in this case may have been influenced by the previous contamination of the studs.

From these results, it was concluded that Butvar B-98 was an ineffective coating for the bronze, but may also have some corrosive effect. The treatment of the serving stand was therefore altered to account for this eventuality. Cleaning of the wood and studs was undertaken using standard cleaning techniques, however, the consolidation procedure was adjusted to take into account the possible corrosive effect of Butvar B-98 on the bronze studs. The serving stand fragments were placed in pouches of silk-screen fabric and immersed in a 10% solution of Butvar B-98 up to a level just below the bronze studs, allowing them to remain above the consolidant solution (fig.6) (Simpson and Spirydowicz 1999). The bronze studs on the serving stand were treated with benzotriazole (BTA) applied by brush, followed by coating with Paraloid B-72 (Simpson and

Figure 6:Won Ng consolidating fragments of stand with Butvar B-98 (Simpson and Spirydowicz 1999)

Spirydowicz 1999).

The final repair and reconstruction of the Tumulus W serving stand took place over a five-year period from 1994 to 1998. The stand was placed on a custom made Plexiglass mount and returned to storage in the newly installed metal cabinets at the Museum of Anatolian Civilizations, where it has remained for the last nine years. Environmental conditions in storage at the museum were monitored with data loggers, revealing a temperature range of 10-27ºC and relative humidity ranging from 30-41.5% RH.* Although there is no climate control in the museum storage area, the fluctuation of temperature and humidity appears to lie within a reasonable range.

Poly(vinyl butyrals)

While the treatment of the stand was successful, the results from the initial testing are surprising. Poly(vinyl butyrals), including Butvar B-98, are known for their excellent stability and one of their primary uses in industry is as a coating for metals (Monsanto Chemical Company 1989). Apart from the possible release of organic acids during chain breakage, very little in the structure of PVBs would indicate any potential harm from its degradation products. PVBs, such as Butvar, are terpolymers composed of the three monomers: poly(vinyl butyral) (PVB), poly(vinyl alcohol) (PVOH) and poly(vinyl acetate) (PVAC). Poly(vinyl butyral), a poly(vinyl acetal), is formed by reacting an aldehyde with a poly(vinyl alcohol) (fig.7). The specific conditions of this reaction, including reactant concentrations, may be controlled in order to determine the proportions of the hydroxyl, acetate, and acetal groups in the resulting polymer (Monsanto Chemical Company 1989). Butvar B-98, for example, is composed of 80% poly(vinyl butyral), 18-20% poly(vinyl alcohol) and 0-2.5% poly(vinyl acetate) (Monsanto Chemical Company 1989). These proportions determine the physical properties of the polymer resin.

* Average temperature and humidity conditions from data loggers in 2004

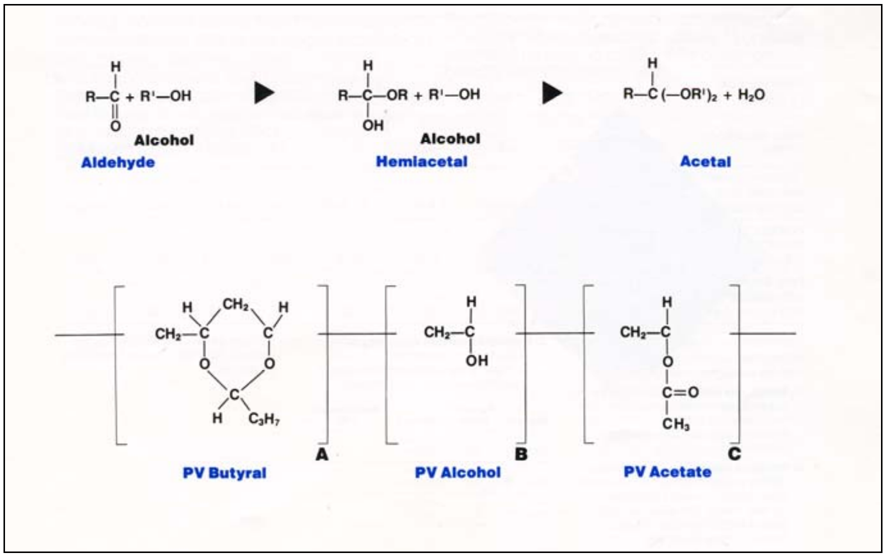

Figure 7: Structure of poly(vinyl butyrals) (Monsanto Chemical Company 1989)

Studies into the photo-degradation of poly(vinyl butyrals) have shown that PVBs are photo-oxidized by both near ultraviolet light and the shorter wavelengths of the visible region (Feller et al. 2007; Reinohl et al. 1981). The glass transition temperature (T_g) is also known to affect the rate and type of degradation resulting from exposure to heat and light. Feller (2007) found that below the glass transition temperature of Butvar B-79, chain breakage resulted from photo-oxidation, while at temperatures above the T_g, cross-linking of the polymer chains was the predominant degradation pathway. As the T_g of Butvar B-98 is between 72ºC to 78ºC, degradation of the polymer would most likely result in chain breakage under normal conditions, this in turn would help maintain the solubility of the polymer in the long term. Induction times for degradation of poly(vinyl butyrals) were also found to be considerably longer at temperatures under the T_g, ensuring the relative stability of Butvar B-98 when kept under normal environmental conditions (Feller et al. 2007).

Analysis of the chemical species released from poly(vinyl butyrals) under accelerated aging conditions has identified butanal (butyraldehyde) and water as the most abundant volatile products (fig.8)(Liau et al. 1996). In addition, very small amounts of butanol and carboxylic acids, specifically acetic and butanoic acid are released (Liau et al. 1996; Dhaliwal and Hay 2002). The amount of acid produced by poly(vinyl butyral) after accelerated light aging, however, was far less than even the small amounts of butyraldehyde produced (Feller et al. 2007). At such low concentrations, the acids released by PVBs would not be expected to induce corrosion on a clean metal substrate.

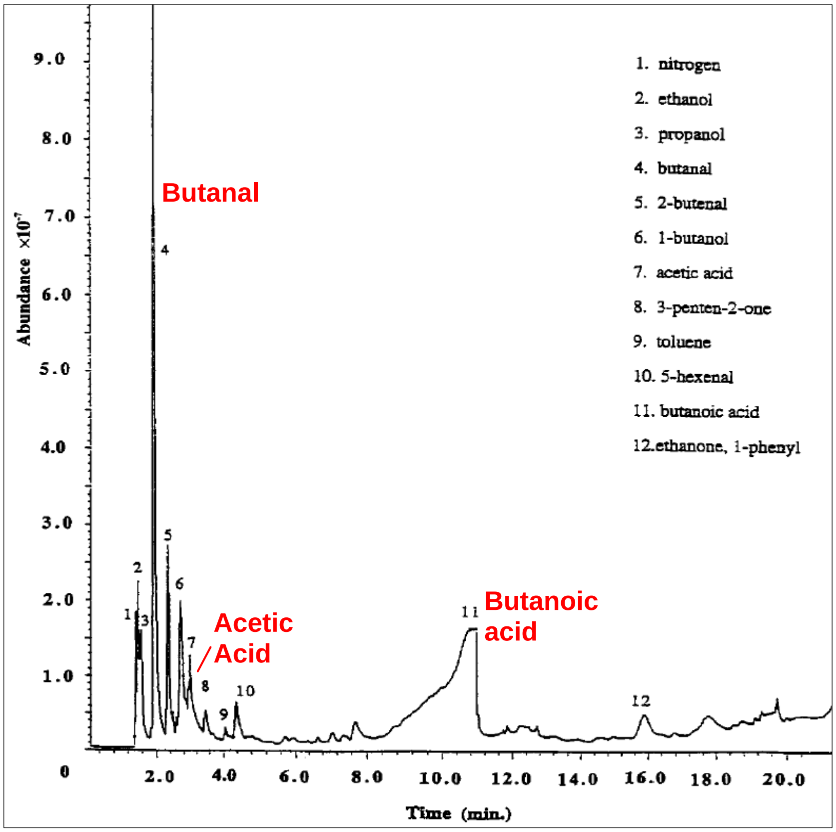

Figure 8: Condensable products of PVB thermal oxidative degradation analyzed by GC-MS, including solvent carriers (Liau et al. 1996)

As chemical research on the structure and degradation of PVBs therefore does not suggest any mechanisms by which poly(vinyl butyral) would interact with bronze to cause corrosion, it was decided that re-testing was necessary to confirm or challenge the results from the original tests. While the conditions of the first experiment appear to have been designed to test the effectiveness of Butvar B-98 and the other polymers as protective coatings, the new testing parameters specifically address the question of whether Butvar B-98 is corrosive to bronze. As the Butvar used to consolidate the serving stand did not theoretically come into direct contact with the studs, but is in close association with them in storage, it was determined that a modified Oddy test, using bronze studs from the Gordion serving stand and bronze coupons, could ascertain the reactions that occur between the materials under accelerated aging conditions. The corrosion produced during testing was then analyzed by XRD and the Butvar B-98 films from the test chambers were analyzed by FTIR. Finally, cold extraction of Butvar B-98 films was performed for pH testing.

2. EXPERIMENTAL PROCEDURE

Samples

A low-tin bronze of roughly the same composition as the bronze studs (6% Sn) was prepared at the Canadian Mint and rolled out into a 1 mm thick sheet. Coupons were cut to measure 26x21x1 mm and prepared for corrosion testing using methods similar to ASTM G1:90 (ASTM 1998) and recommended by Faltermeier (1999). A hole was drilled into each coupon, the surfaces were then sanded with 600 grit sandpaper, rinsed in acetone, and allowed to air dry in the fume hood. Sample numbers were engraved on one side of each coupon using an electric engraver's tool. The coupons were then individually photographed and weighed.

The six bronze studs from the Gordion Serving stand, which were covered in burial soil and encrustations, were weighed and photographed before undergoing cleaning. Each stud was cleaned mechanically using a pin tool, ethanol, and a stiff bristled brush. Extensive corrosion was present on all of the studs and small areas of bronze disease were visually identified on three. The soil filling the heads of the studs was found to be sticky and plasticized, due most likely to the application of Alvar after excavation. In addition, woody structures were found on two of the six studs, likely the remnants of the serving stand itself. All of the material removed from the studs was placed in sample vials in case future analysis may be required. Each stud was then degreased in acetone, photographed and re-weighed.

Oddy Test

The Oddy test chambers were assembled by suspending triplicate sets of bronze coupons and bronze studs on nylon monofilament in flint glass jars. 2 grams of Butvar B-98 film, cast from a 15% solution in 60/40 ethanol/toluene, was added to half of the chambers along with glass vials filled with distilled water and stoppered with cotton wool. The chambers were then sealed and placed in an oven at 60˚ Celsius for 28 days. After testing, each coupon and stud was removed, photographed, and re-weighed

After the coupons and studs were removed from the Oddy test jars, surface corrosion was sampled by scraping off the corroded surfaces with a scalpel. The powdered corrosion products were then analyzed by X-ray diffraction by Alan Grant in the Department of Geological Science and Engineering at Queen's University. The samples were scanned with a Philips (now PANalytical) X'Pert Pro MPD diffractometer fitted with an X'Celerator high speed strip detector. Samples were mounted as fine powder on Si zero background plates. Analysis was done using Co $K\alpha$ radiation (Fe filtered), 0.02 rad incident beam soller, 15 mm mask, ½º divergence slit, 1º anti-scatter slit, and 0.02º diffracted beam soller. Count time was 45 sec at 0.02º 2θ increments scanned from 5º to 115º 2θ with sample rotation at 2 sec/revolution. PanAlytical HighScore software was used for phase identification with the Powder Diffraction File Release 2001 database published by International Centre for Diffraction Data in 2001.

After the samples were removed and analyzed, the remaining corrosion on the coupons was removed by immersing them in a 1:1 solution of hydrochloric acid and water following ASTM G1-90 for measuring corrosion of metals (ASTM 1998). The coupons were once again photographed and weighed. In addition, small pieces of the Butvar films from the Oddy test chambers were sampled for analysis by FTIR by removing small strips of film with a scalpel.

pH

pH testing of dried Butvar B-98 films was performed following the ASTM testing methods for hydrogen ion concentration of dry adhesive films (1982). Down et al. (1996) have also used this method successfully at CCI to help determine the suitability of different adhesives for use in conservation. The films were cut into small pieces and 2g of sample were weighed into three glass vials. Each vial, including an empty control, were filled with 10 ml of deionized water, shaken, and allowed to sit for 72 hours to allow the extraction to take place (fig.9). The pH of each sample was then measured every 24 hours until stabilization of the solution pH occurred.

Figure 9: Control vial and test vials for pH testing with Butvar films

3. RESULTS

	#	Before Aging (g)	After HCl (g)	Weight Change (g)	AVG loss (g)	STDEV
No Butvar	25	4.1465	4.1366	-0.0099	-0.0045	0.0047
	26	4.0688	4.0671	-0.0017		
	27	4.2095	4.2076	-0.0020		
Butvar	28	4.6937	4.6901	-0.0036	-0.0076	0.0035
	29	4.5279	4.5185	-0.0094		
	30	4.3399	4.3302	-0.0097		

Table 1: Weight changes of bronze coupons after Oddy test

#	Butvar	Day 1	Day 2	1 Week	Day 12	1 Month
25	No Butvar	No change	Darkening	Dark tarnish	Dark tarnish	Dark tarnish, some light green corrosion
26	No Butvar	No change	Darkening	Dark tarnish	Dark tarnish	Dark tarnish on part of coupon
27	No Butvar	No change	Darkening	Dark tarnish	Dark tarnish	Dark tarnish on part of coupon
28	Butvar	Mottled darkening	Darkening	Dark tarnish	Dark tarnish	Dark tarnish
29	Butvar	Mottled darkening	Darkening	Dark tarnish	Dark tarnish	Dark tarnish
30	Butvar	Mottled darkening	Darkening	Dark tarnish	Dark tarnish and Green Corrosion	Dark tarnish and has areas of green corrosion

Table 2: Visual observations of the coupons that underwent Oddy testing over one month

	Stud	Before (g)	After (g)	Weight Change (g)	AVG change (g)	STDEV
Butvar	1	1.0629	1.0654	0.0025	0.0041	0.0035
	2	0.9902	0.9984	0.0081		
	5	0.9701	0.9719	0.0018		
No Butvar	3	0.7284	0.7323	0.0040	0.0047	0.0011
	4	0.9041	0.9084	0.0042		
	6	1.0499	1.0559	0.0060		

Table 3: Weight changes of bronze studs after Oddy test

	Stud	Before cleaning	After 24 hours	After Oddy test
Butvar	1	No bronze disease	Very small amount of bronze disease	Very small amount of bronze disease
	2	No bronze disease	Very small amount of bronze disease	Very small amount of light green crystals on exterior
	5	Bronze disease present	Largest amount of bronze disease	Several large spots of bronze disease on exterior
No Butvar	3	No bronze disease	Small amount of bronze disease	Large amount of bronze disease on outside of head, a small amount on inside as well
	4	Some bronze disease	Small amount of bronze disease	Large amount of bronze disease on outside and inside of head
	6	No bronze disease	Small amount of bronze disease	Virtually no bronze disease although a film of light colored corrosion is present on interior

Table 4: Visual observations of the studs that underwent Oddy testing over one month

The average weight changes after Oddy testing of the coupons exposed to Butvar and the coupons not exposed to Butvar are reported in table 1 along with the standard deviations. These values were calculated from the weights of the coupons before Oddy testing and after removal of the corrosion in HCl at the end of testing. The visual observations of these coupons during and after testing are reported in table 2. The average weight changes after Oddy testing of the studs exposed to Butvar and the studs not exposed to Butvar are reported in table 3. These values were calculated from the weights of the studs before Oddy testing and after Oddy testing. The visual observations of the studs before, during, and after testing are reported in table 4.

XRD Analysis

Diffractograms from XRD analysis of the corrosion products from the Oddy test coupons 25 through 30 are included as appendix A. These diffractograms include the identified phases and their characteristic series of peaks. The major phases identified in all of the samples, except for coupon 26, were bronze and tenorite (CuO), or cupric oxide. The diffractogram of the corrosion from coupon 26 indicated the presence of bronze only. This may be due to the fact that only a very small amount of corrosion was removed from coupon 26, which may not have produced a strong enough signal for XRD analysis. The small amount of bronze in the sample is due to the sampling method of scraping the coupon surface.

Diffractograms from XRD analysis of the corrosion products on studs 3 and 5 identify the same corrosion products in both cases (fig.10). Stud 3 was exposed to Butvar B-98 during the Oddy test while stud 5 was not. The phases identified on both studs were atacamite ($Cu_2Cl(OH)_3$) and clinoatacamite ($Cu_2(OH)_3Cl$).

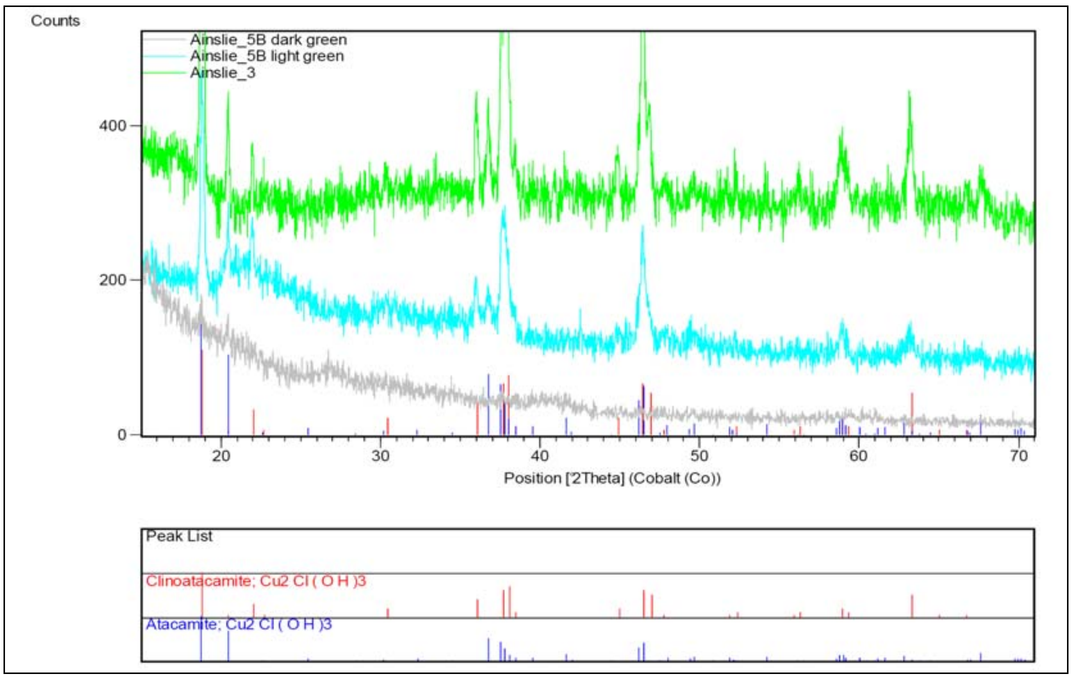

Figure 10: XRD diffractogram of the corrosion from stud 5, which was not exposed to Butvar B-98 and stud 3, which was exposed to Butvar B-98

FTIR Analysis

FTIR spectra were obtained for four samples of Butvar B-98 film (fig.11). The control sample was taken from a freshly cast film of Butvar B-98. The sample from Jar 2 was aged for 45 days under the conditions of the Oddy test while the sample from Jar 3 was aged for 28 days under the conditions of the Oddy test. The sample from Jar 4 was aged in an acidic atmosphere (pH of 3.5) for one month at 25˚C.

The broad band centered near 3400 cm^{-1} in all four spectra is due to water. The weak peak at 2736 cm^{-1} is due to the aldehyde group and the weak peak at 1735 cm^{-1} is due to the carbonyl group of aldehyde. The weak sharp peak at 732 cm^{-1} is most likely due to solvent, since it is absent from the spectra of the heated samples.

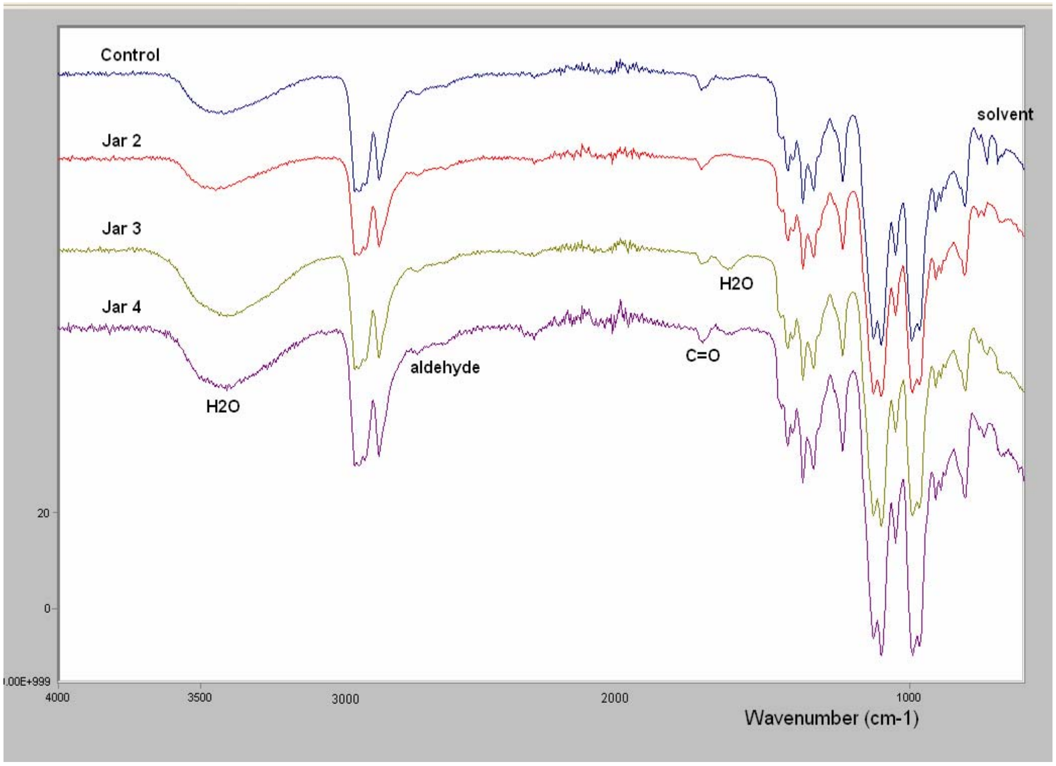

Figure 11: Overlay of the FTIR spectra of four Butvar B-98 cast film samples after undergoing aging in varying conditions

pH

Results from pH testing over 144 hours are included as table 5. The pH of the deionized water was measured at 6.7 before testing, and after 144 hours was found to be 7.05. The solutions in vials 1-3, which contained deionized water and Butvar B-98 film extraction, all remained within a pH range of 6.54 – 6.97.

Vial #	Initial	72 hours	96 hours	120 hours	144 hours
Control vial	6.70	6.70	6.90	6.87	7.05
Vial 1		6.82	6.94	6.93	6.83
Vial 2		6.79	6.78	6.54	6.61
Vial 3		6.97	6.84	6.93	6.88

Table 5: pH measurements of Butvar B-98 cold extraction solutions and a control of deionized water

4. DISCUSSION

For corrosion testing, weight changes were assumed to correlate with extent of corrosion, following previous studies. Weight gain may be used to indicate the degree of corrosion in the samples as the formation of corrosion products will increase the overall weight of the coupon (Golfomitsou and Merkel 2004). The loss of weight after removal of corrosion in HCl is also taken to correlate with the degree of corrosion following ASTM G1-90 (ASTM 1998). A greater loss of weight is understood to correspond with the development and subsequent removal of a larger amount of corrosion.

Oddy Test Coupons

The differences in the weight changes observed in the Oddy test coupons exposed to Butvar and those that were not exposed to Butvar B-98 were within the standard deviations calculated from the triplicate sets of samples (see fig.12). This is true for both the weight changes from before and after testing and the weight changes after removal of corrosion in HCl. The greater variability in the triplicate sets than between the coupons exposed to Butvar B-98 and not exposed to Butvar B-98 indicates that the Butvar B-98 film had little to no effect on the corrosion of the metal under the Oddy test conditions.

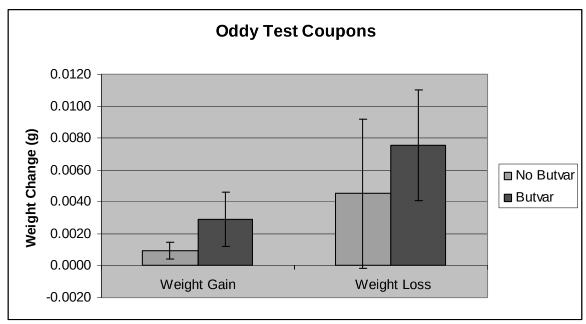

Figure 12: Avg. weight gain of coupons after testing and weight loss after HCl immersion

The Oddy test was originally designed to test the suitability of materials to be used in close association with metal artifacts (Oddy 1973). Although the test can be relatively subjective, it allows for easy determination of unsuitable materials should a large difference in the amount and type of corrosion occur between the samples exposed to and those not exposed to the test material. In this case, a significant difference was not found to occur between the coupons exposed to Butvar B-98 and those that were not exposed to Butvar B-98 as all coupons exhibited a similar degree of corrosion at the end of testing (fig.13). The slight variation noted between coupons and jars was expected due to the inherent variability in the test. It may therefore be concluded that Butvar B-98 is a suitable material to use in association with bronze objects.

Figure 13: Before and after photos of coupon #25 not exposed to Butvar (top), and coupon #29 exposed to Butvar (bottom)

The same corrosion product, tenorite, was identified by XRD on both the coupons exposed to Butvar B-98 and those not exposed to Butvar B-98 (fig.14). Tenorite, or cupric oxide, is the expected corrosion product for bronze in the presence of water and heat. Tenorite, which generally ranges from black to gray, is responsible for the dark tarnish on the coupons (Selwyn 2004). XRD did not identify other phases that could account for the green corrosion, likely because of the relative abundance of tenorite. The identification of the same corrosion product on all of the coupons, however, supports the conclusion that Butvar does not significantly influence the corrosion of bronze.

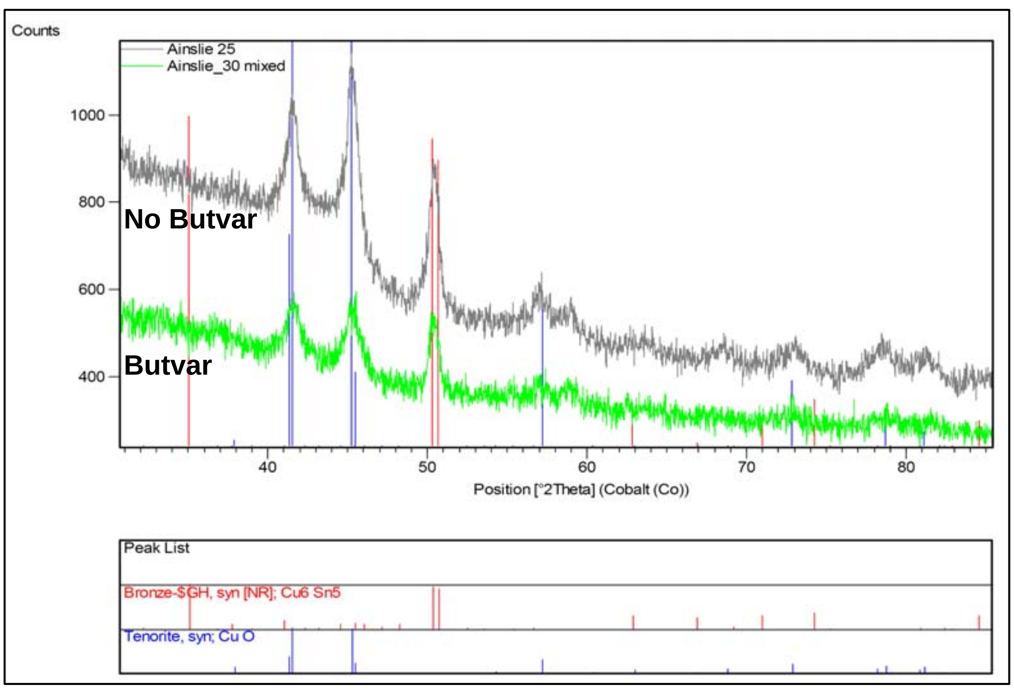

Figure 14: XRD diffractogram of corrosion from coupon 25 and coupon 28

Oddy Test Studs

The difference in the weight changes observed in the Oddy test studs exposed to Butvar and those that were not exposed to Butvar was within the standard deviations calculated from the triplicate sets of samples (fig.15). Both the studs exposed to Butvar and those not exposed to Butvar developed light green corrosion after one month of Oddy testing (fig.16). This corrosion was identified by XRD to be atacamite and clinoatacamite (fig.10). These copper chloride hydroxide corrosion products develop only when chloride-containing species are present. The determining factor in the development of corrosion during testing therefore appears to be the previous contamination of the metal with chlorides. The presence of Butvar B-98, on the other hand, did not appear to influence either the type or amount of corrosion that developed on the studs.

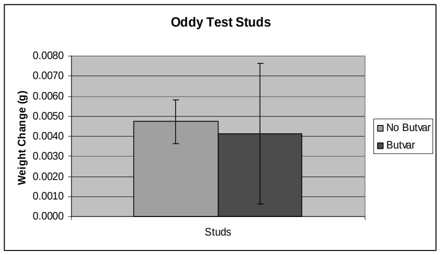

Figure 15: Average weight change of the studs exposed to Butvar and not exposed to Butvar

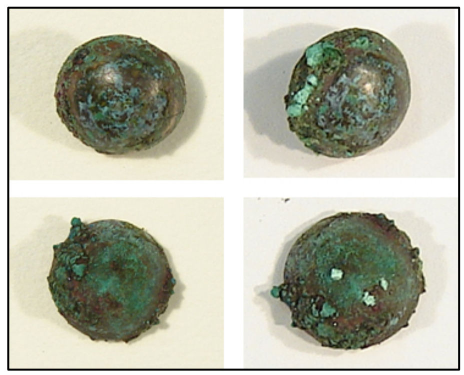

Figure 16: Before and after photos of stud 3 not exposed to Butvar (top), and stud 5 exposed to Butvar (bottom)

FTIR

FTIR analysis of the Butvar films from the Oddy test jars and acidic atmosphere indicates that little change occurred to the films due to aging under testing conditions. Changes in FTIR spectra have been used in other studies to demonstrate the evolution of volatile products and changes occurring to the polymer structure due to heat or light (Dhaliwal and Hay 2002; Reinohl et al. 1981; Liau et al. 1996). The structural changes that have been identified by FTIR in the past, however, are found to occur after exposure to far more extreme conditions than those of the Oddy test. It was therefore not surprising that little to no change was seen in the IR spectra. The same peaks were present after aging as before, except for the sharp peak at wavenumber 732, which was due to the solvent that evaporated during heating. As no change in the composition of the polymer occurred, it is likely that little to no volatile products were released. This is consistent with the weight and observational results, which indicate that the presence of the Butvar B-98 films caused no addition reactions with the bronze, such as would occur if significant amounts of harmful volatiles had been released.

pH

The Butvar B-98 films that underwent pH testing after 144 hours of cold extraction were within a pH range of 6.5 to 7. This indicates that fresh films of Butvar are neither acidic nor alkaline. While neutral pH (7) is ideal, researchers at CCI place the acceptable range for pH between 5.5 and 8 (Down et al. 1996). The pH of fresh Butvar B-98 film falls within this range and is therefore not expected to cause any pH specific deterioration when in contact with metals. Only fresh Butvar B-98 films, however, were tested in this study and it is therefore recommended that further testing be performed on dark aged and light aged films to ensure that the pH remains within an acceptable range.

5. CONCLUSION

Contrary to the conclusions drawn from initial testing of Butvar B-98 in 1991, the results from this research indicate that Butvar B-98 does not significantly affect bronze under accelerated aging conditions. Based on weight and observational results, Butvar B-98 was not found to corrode the coupons and studs to any greater degree. Analysis of the resulting corrosion products using XRD confirmed that exposure to Butvar B-98 did not affect the type of corrosion that developed on bronze as the phases identified on the samples exposed to Butvar B-98 and not exposed to Butvar B-98 were identical.

The current information available on the structure and degradation of Butvar B-98 and other poly(vinyl butyrals) also indicates that it is unlikely that Butvar B-98 would have a corrosive effect on bronze under typical environmental conditions. Butvar B-98 is a relatively stable material that releases minimal corrosive degradation products only after exposure to extreme temperatures and UV light. The results from FTIR analysis of the Butvar B-98 films after Oddy testing show no change to the polymer structure, confirming that there is no chemical mechanism by which Butvar B-98 could cause corrosion on the associated bronze coupons.

The results from this study suggest that Butvar B-98 is safe to use in association with bronze and likely with other metals as well. The bronze studs from the Tumulus W serving stand are therefore not considered at risk from any corrosive interactions with the Butvar B-98 used to consolidate the stand. A greater concern for the bronze studs on this piece is the presence of chlorides, which has been demonstrated during testing. The treatment of the individual studs with BTA, a corrosion inhibitor, and their subsequent coating with Paraloid B-72, however, will most likely protect the studs from further deterioration while in storage at the Museum of Anatolian Civilizations.

While Butvar B-98 has proven safe to use on composite artifacts that contain bronze, its effectiveness as a protective coating for metals has not yet been fully addressed. Although other materials may prove to be more successful as protective coatings for metals, Butvar B-98 would be far more convenient a choice as a 2-in-1 consolidant and coating for composite wood and metal artifacts. As this study evaluated only the potential corrosivity of Butvar B-98, it is suggested that further testing be carried out to determine whether Butvar B-98 or the other poly(vinyl butyrals) can function effectively as coatings for metal components of wooden artifacts.

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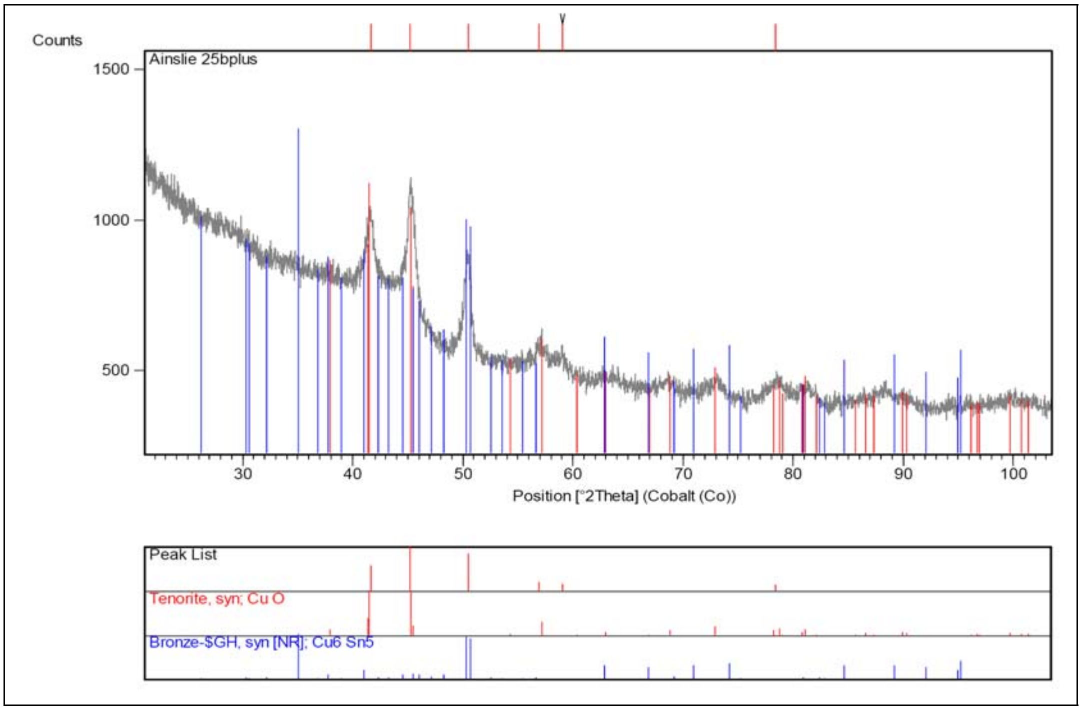
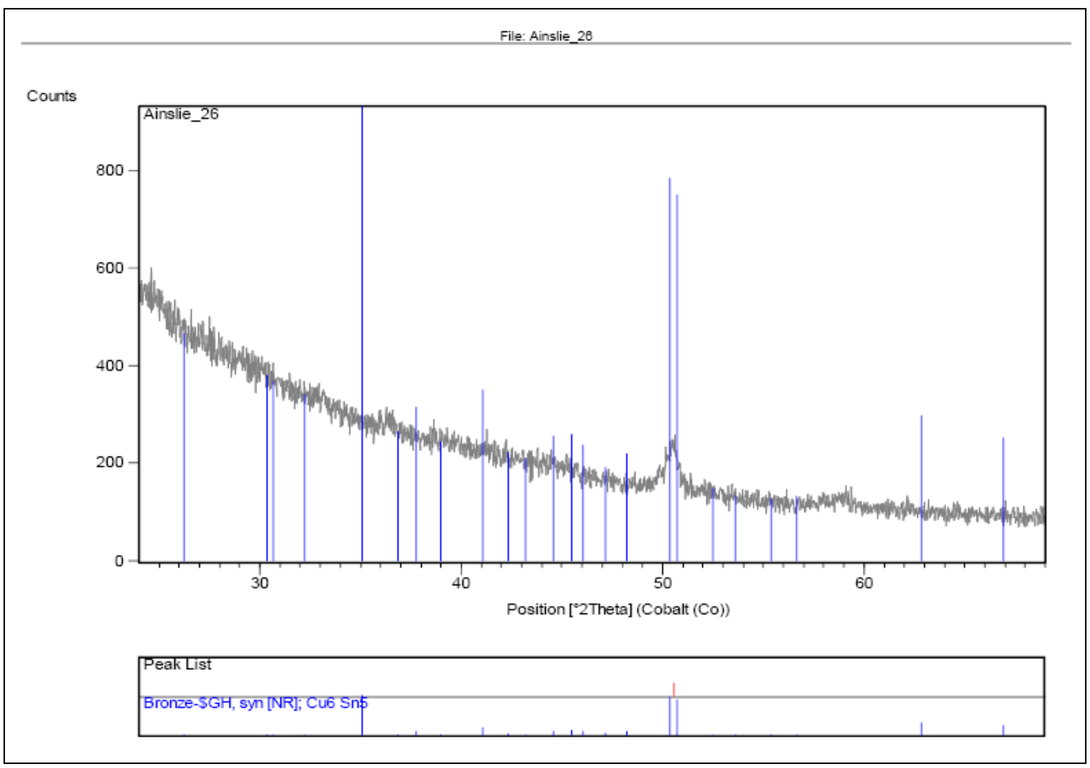
APPENDIX A: Diffractograms of corrosion from Oddy test coupons



Coupon 25



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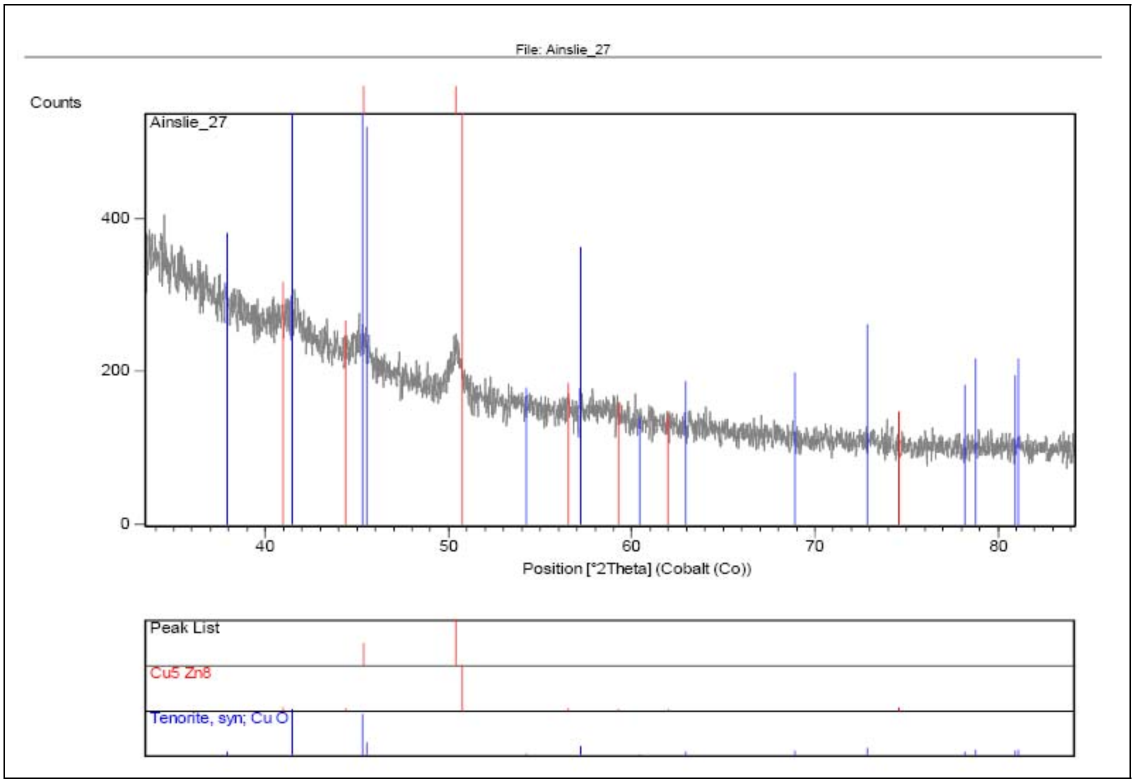

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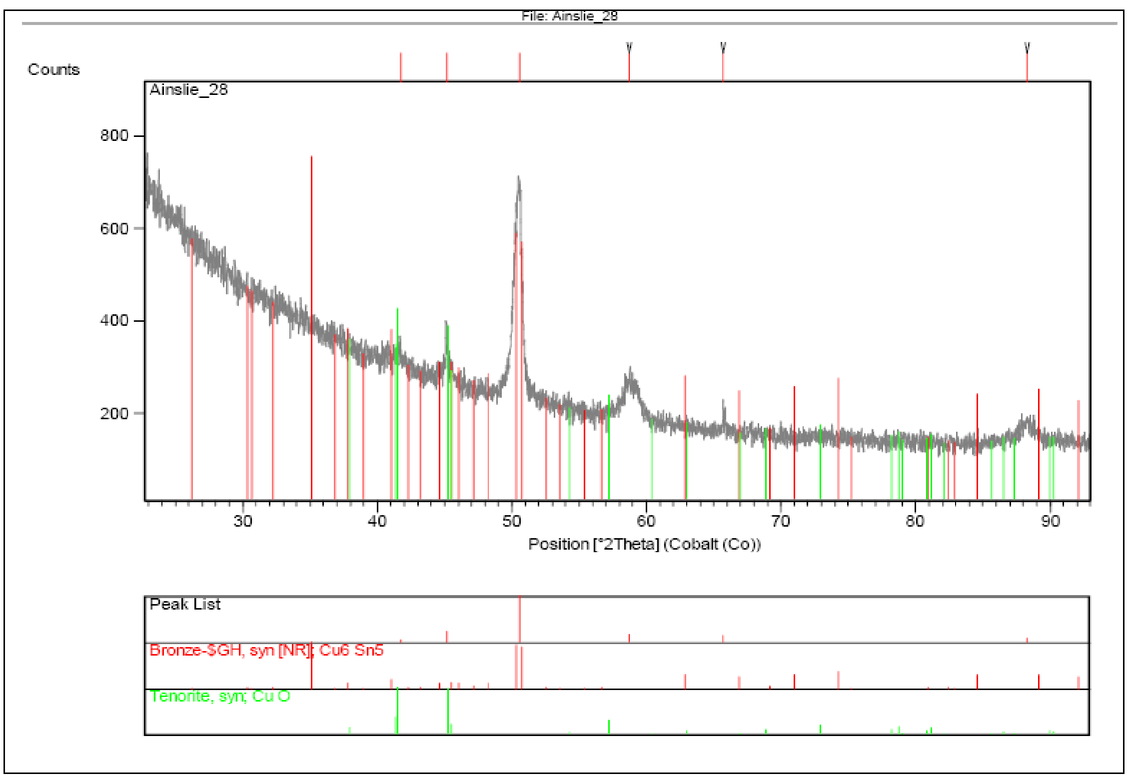

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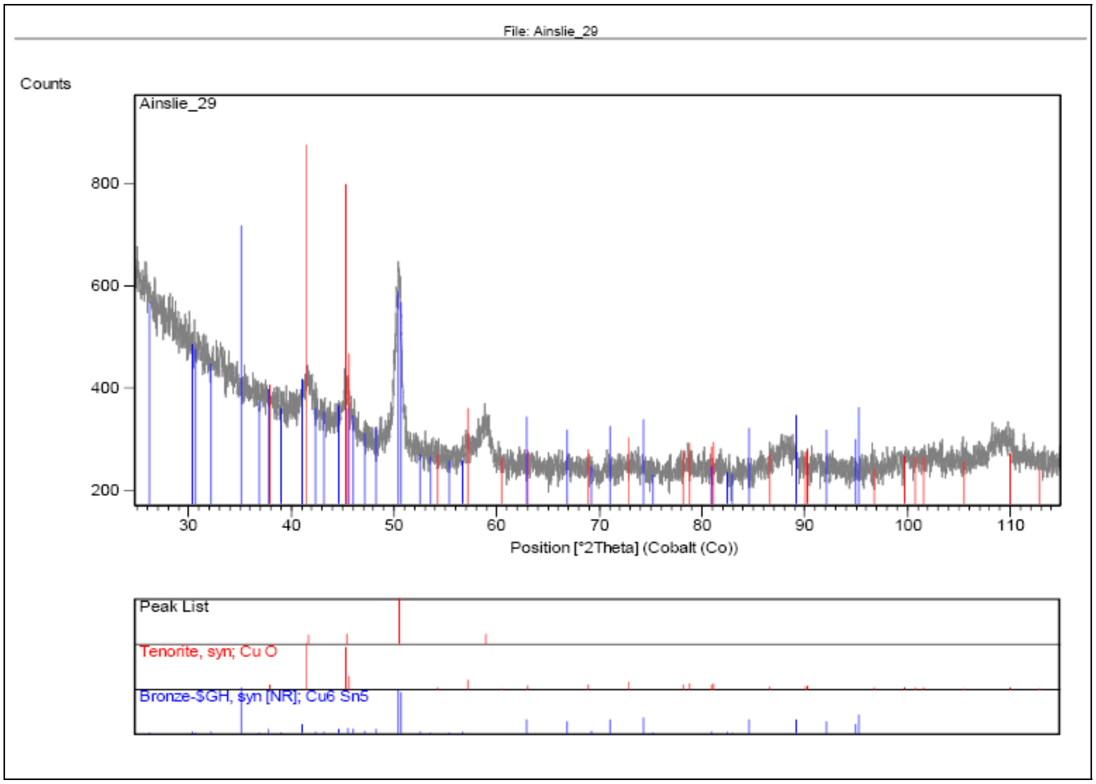

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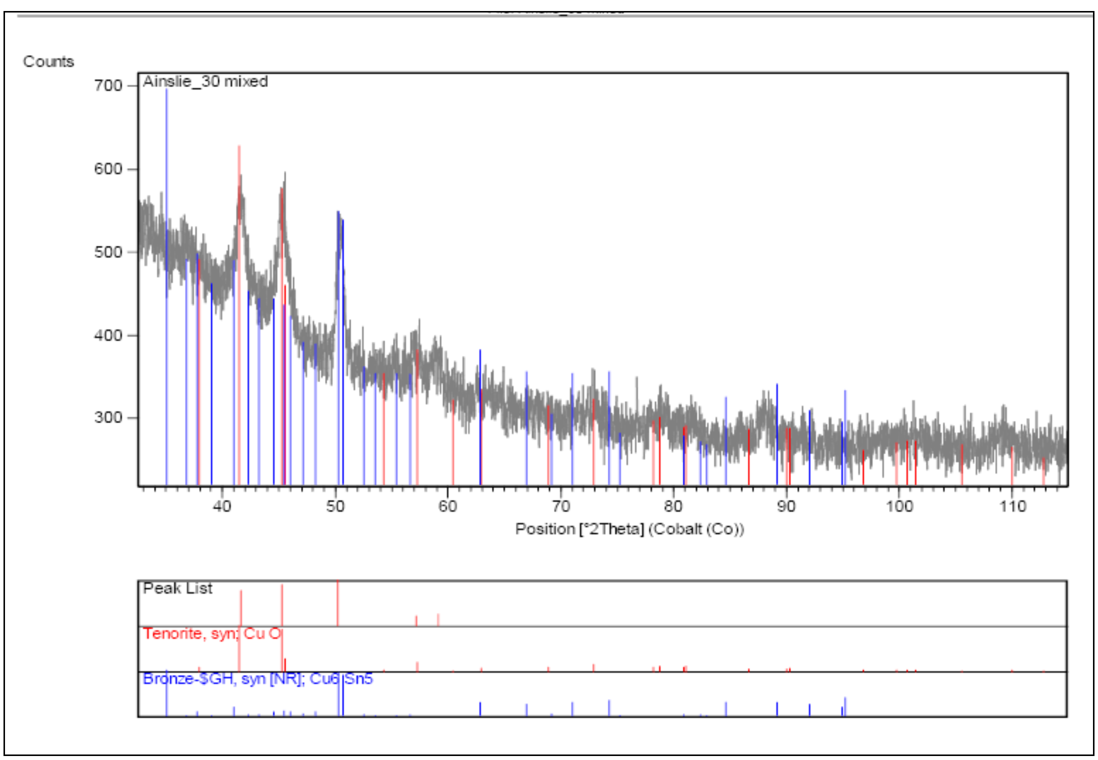
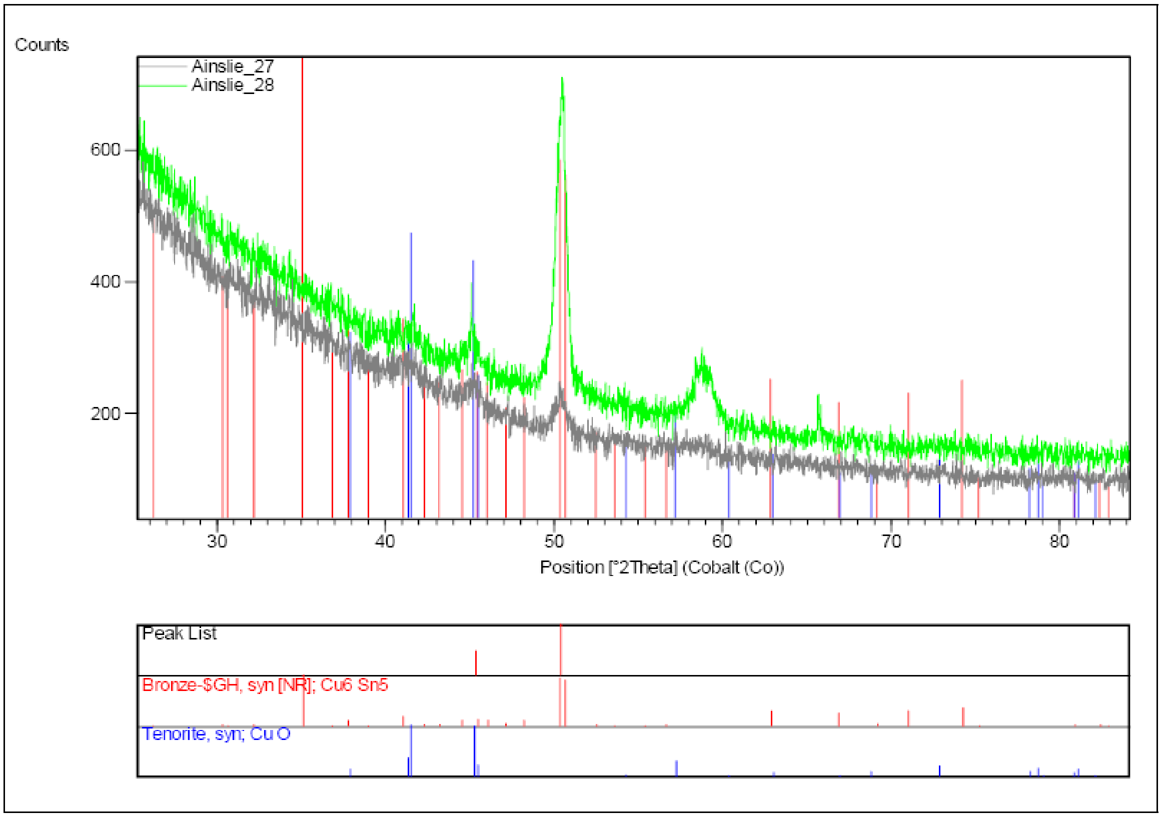


Coupon 30



Coupons 27 and 28