A Study of Butvar and its Effects on Bronze

by Ainslie C. Harrison

Introduction

While conservators have a wide range of thoroughly tested materials available to them for use with metals, situations involving composite objects require consolidants and coatings known to be compatible with both the organic and metal components. The poly(vinyl buytrals), like Butvar, have been used frequently as consolidants, adhesives, and filling materials for wood, leather, and other organics, but reservations remain about their suitability for metals.

Questions regarding the effects of Butvar on metals arose in 1990 when treatment of a composite wood and bronze serving stand began at the Gordion Furniture Project in Ankara (fig.1) (Simpson and Spirydowicz 1999). The fragmentary stand, believed to be from the 8th c. BCE, is one of many exquisitely carved wooden furniture pieces found in the burial mounds at the ancient Phrygian capital. The stand is unique, however, in that it is covered on top with small bronze studs.

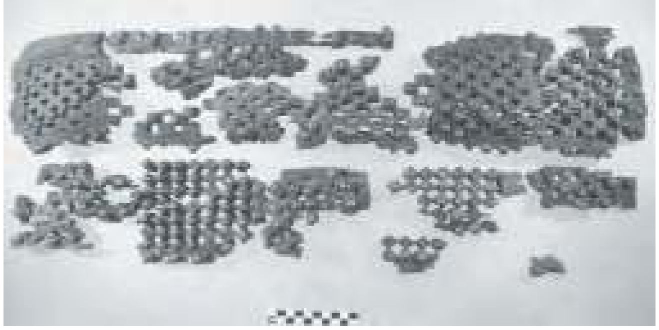

Figure 1. Tumulus W serving stand after conservation (Simpson and Spirydowicz 1999)

Conservators chose Butvar B-98 to consolidate the weak, desiccated boxwood as extensive testing and previous use on other furniture pieces from Gordion had shown it to be an effective consolidant for this kind of material.

The serving stand fragments were partially immersed in a 10% solution of Butvar B-98 in 60/40 ethanol/toluene by maintaining the consolidant level just below the surface with the bronze studs. Contact between the Butvar and studs was avoided mainly because of initial tests indicating that the Butvar may have some corrosive effect on the bronze (Ng 1992). The serving stand was then reconstructed over several years, placed on a custom made Plexiglas mount, and returned to storage at the Museum of Anatolian Civilizations in Ankara where it remains.

While no visible deterioration of the serving stand has occurred to date, ongoing concern over the potential corrosivity of Butvar prompted further research at Queen's University into its effect on bronze. While an in-depth description of the project and results may be found elsewhere (Harrison 2008a,b), a summary of the findings are presented in this article.

Poly(vinyl butyrals) in Conservation

Around the time the Gordion Furniture Project began, several studies pointed to the polyvinyl butyrals (PVB), such as Butvar, as ideal consolidants for dry wood. Extensive research on dry wood consolidants at the Canadian Conservation Institute (CCI) indicated that the PVBs 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; Barclay 1981). Virtually no shrinkage or expansion was observed in the wood treated with Butvar, and only minimal color change was found to occur. Butvar also has very good adhesive properties, a relatively high glass transition temperature (T_g), and its viscosity can be adjusted by varying the solvent carrier. The testing and use of Butvar B-98 in conservation has 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; Paterakis 1996; Toutloff 1999; Spirydowicz et al. 2001).

Poly(vinyl butyral) Structure and Degradation

PVBs, 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). PVBs are terpolymers composed of the three monomers: poly(vinyl butyral) (PVB), poly(vinyl alcohol) (PVOH) and poly(vinyl acetate) (PVAC). PVB is formed by reacting an aldehyde with a PVOH under specific conditions that control the resulting proportions of hydroxyl, acetate, and acetal groups (fig.2). Butvar B-98, for example, is composed of 80% PVB, 18-20% PVOH, and 0-2.5% PVA (Monsanto Chemical Company 1989). These proportions in turn determine the physical properties of the polymer resin.

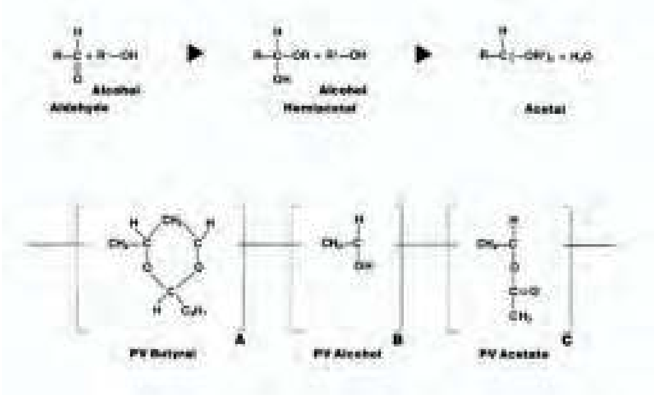

Figure 2. Structure of poly(vinyl butyrals) (Monsanto Chemical Company 1989)

Studies into the photo-degradation of PVBs reveal very good long-term light stability (Feller et al. 2007; Reinohl et al. 1981). The T_g, however, is known to affect the rate and type of degradation resulting from exposure to heat and light. Feller et al. (2007) found that at temperatures above the T_g of Butvar B-79, cross-linking of the polymer chains occurred after exposure to UV radiation, while at temperatures below T_g, chain breakage resulted from photo-oxidation, thus maintaining the polymer's solubility when kept under normal temperature conditions. Induction times for degradation of PVBs were also found to be considerably longer at temperatures below T_g leading Feller et al. (2007) to estimate that, under typical museum conditions, PVBs may go 113 years before onset of weight loss and other degradation mechanisms.

Analysis of the chemical species released from PVBs has identified butanal (butyraldehyde) and water as the most abundant volatile products from thermal oxidative degradation (Liau et al. 1996). While butyric acid was also found to be a product of PVB degradation, it is produced in much smaller quantities (Liau et al. 1996; Dhaliwal and Hay 2002). Feller et al. (2007), for example, reported just 1 mol of acid liberated for every 70 mol of aldehyde after 455 hours of exposure under UVA lamps (fig.3).

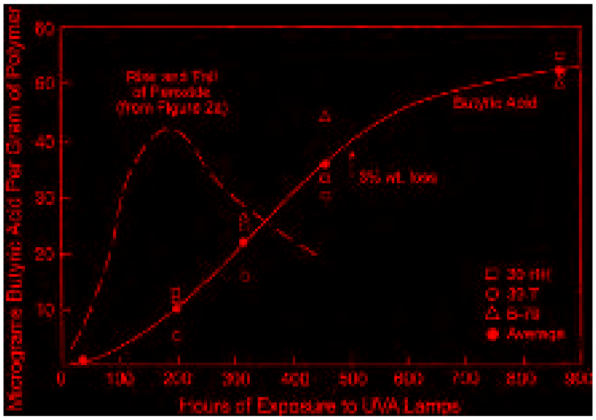

Figure 3. Evolution of butyric acid from PVBs exposed to UVA Lamps (Feller et al. 2007)

Experimental

As the bronze studs on the serving stand did not come into direct contact with the Butvar consolidant, a modified Oddy test was used to determine the possible interactions of the materials when in close proximity. Bronze coupons were made with a similar composition to the bronze studs (6% Sn and 94% Cu), cut from one mm thick sheet that was prepared and rolled at the Canadian Mint. The coupons and studs were suspended in sealed jars, half of which contained cast films of Butvar B-98, and were aged at 60° Celsius for one month at high humidity. The corrosion produced on the Butvar exposed samples and controls during Oddy testing was then scraped off and analyzed by XRD.[1] The remaining corrosion was cleaned from the coupons with HCl for weight measurements (ASTM 2005), and the Butvar films were removed from the test jars and analyzed by FTIR.[2]

Tests for pH of dried Butvar B-98 films were also performed following ASTM D 1583-61 (1982), a method also used by Down et al. (1996) at CCI to help determine the suitability of different adhesives for use in conservation. Small pieces of Butvar films (2g) were added to vials of water and measurement taken daily until stabilization of the solution pH occurred.

Results and Discussion

All of the Oddy test coupons were visually determined to have corroded by the end of testing. There was no significant difference in the appearance of the corrosion between coupons exposed to Butvar and the controls (fig.4).

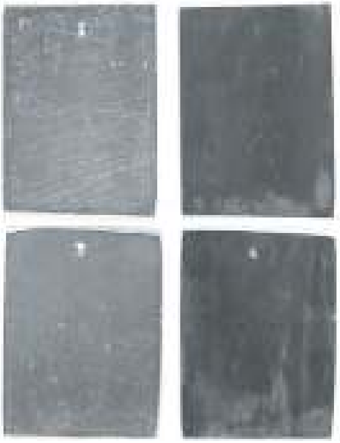

Figure 4.
Before and after photos of control coupon #25 (top), and coupon #29 exposed to Butvar (bottom)

Weight measurements and XRD analysis confirmed the visual results. The difference in weight loss after Oddy testing between the controls and the coupons exposed to Butvar was within the standard deviation, indicating that the same amount of corrosion occurred to both (table 1).

Table 1. Weight changes of bronze coupons after Oddy test

	#	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		

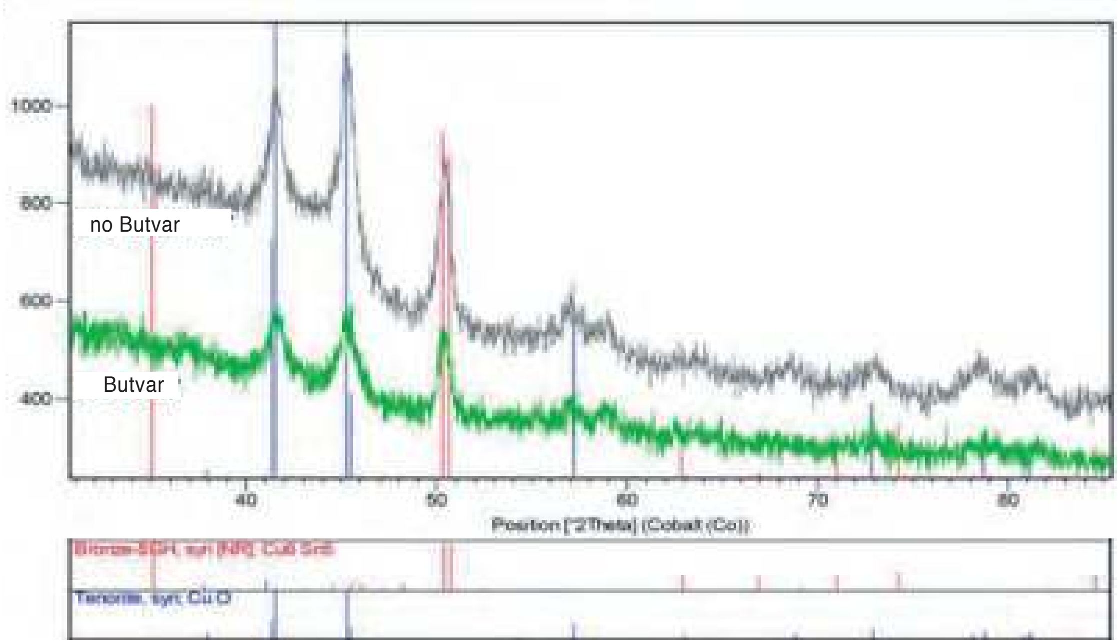

Figure 5. Diffractogram of corrosion from coupons 25 (control) and 30

Similarly, XRD confirmed that tenorite was produced on both types of coupons, which suggests that the copper was oxidized in each case via the same corrosion mechanism (fig.5).

The Oddy test results for the bronze studs was similar to that of the coupons in that no difference was noted between the control studs and those exposed to Butvar (fig.6).

Figure 6. Before and after photos of stud 3 not exposed to Butvar (top), and stud 5 exposed to Butvar (bottom)

All of the studs developed bronze disease by the end of testing, which was confirmed by the presence of atacamite ($Cu_2Cl(OH)_3$) and clinoatacamite ($Cu_2(OH)_3Cl$) identified by XRD. Weight results also indicate that the control studs corroded to the same degree as the studs exposed to Butvar (table 2). Most likely, previous contamination of the studs with chlorides was the main catalyst for corrosion in this case. No significant change was noted in the FTIR spectra between the Butvar films before and after Oddy testing except for the disappearance of a solvent peak due to evaporation. Also, the pH of the Butvar films, measured after 144 hours of extraction, was found to be within an acceptable pH range of 6.6 to 7. In summary, there was no indication that the Butvar films in these tests released any corrosive product that could damage bronze.

Conclusion

Experimental work has shown no evidence that fresh films of Butvar B-98 release volatile products corrosive to bronze under the accelerated aging conditions of the Oddy test. This is supported by testing of the Butvar films by FTIR, cold extraction pH testing, and gravimetric and XRD analysis showing the similarity in type and amount of corrosion between controls and bronze coupons exposed to Butvar.

Table 2. Weight changes of bronze studs after Oddy test

	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		

The literature indicates that PVBs are highly stable and emit very small amounts of butyric acid only after exposure to extreme UV light and thermal conditions. Although Feller et al. (2007) suggested a comfortable induction period before degradation of PVBs in the museum environment of over 100 years, this figure allows for an average light exposure of 323 lux. While consolidated objects in storage, like the Gordion serving stand, have virtually no light exposure and can likely expect a longer period before PVB degradation begins, estimates based on accelerated aging tests are problematic as they assume linear extrapolation of laboratory-derived arrays that may have more complex form over longer timescales. The best course of action, even where testing indicates long-term stability of the material, is continued monitoring and maintenance of good environmental conditions in storage.

Fortunately, the Gordion serving stand is kept under ideal RH and temperature conditions at the Museum of Anatolian Civilizations. This is especially important as testing of the loose bronze studs in this study indicated the presence of chlorides. The studs on the serving stand, however, were treated with BTA and coated with Paraloid B-72 during the initial conservation treatment, which so far appears to have been successful in preventing further corrosion.

Notes

1. XRD was carried out by Alan Grant in the Department of Geological Science and Engineering at Queen's University.
2. Herbert (Gus) Shurvell carried out FTIR analysis of the Butvar films in the Art Conservation Department at Queen's University.

REFERENCES

ASTM. 1982. D 1583-61: Standard test method for hydrogen ion concentration of dry adhesive films. *Annual Book of ASTM Standards* 22:477-478.

———. 2005. Preparing, cleaning, and evaluating corrosion test specimens, GI-81; Conducting atmospheric corrosion tests on metals, G50-76. In *Annual book of ASTM Standards: Wear and erosion*. Philadelphia: American Society for Testing and Materials.

Barclay, R. 1981. Wood consolidation on an eighteenth century English fire engine. *Studies in Conservation* 26 (4):133-139.

Battram, A. 1991. A study of Butvar B98 as a consolidant for degraded wood, MAC research project report, Queen's University, Kingston, Ontario.

Carlson, S. M., and A. P. Schniewind. 1990. Residual solvents in wood-consolidant composites. *Studies in Conservation* 35 (1):26-32.

Dhaliwal, A. K., and J. N. Hay. 2002. The characterization of polyvinyl butyral by thermal analysis. *Thermochimica Acta* 391:245-255.

Down, J. L., M. A. MacDonald, J. Tetreault, and R. S. Williams. 1996. Adhesive testing at the Canadian Conservation Institute-an evaluation of selected poly(vinyl acetate) and acrylic adhesives. *Studies in Conservation* 41:19-44.

Feller, R. L., M. Curran, V. Colaluca, J. Bogaard, and C. Bailie. 2007. Photochemical deterioration of poly(vinyl butyral) in the range of wavelength from middle ultraviolet to the visible. *Polymer Degradation and Stability* 92:920-931.

Grattan, D. W. 1980. Consolidants for degraded and damaged wood. In *Proceedings of the Furniture and Wooden Objects Symposium*. Ottawa: CCI.

Grattan, D. W., and R. L. Barclay. 1988. A study of gap-fillers for wooden objects. *Studies in Conservation* 33 (2):71-86.

Harrison, A. 2008a. The effects of Butvar B-98 on bronze. In *ANAGPIC Student Papers Presented at the 2008 Annual Student Conference Hosted by New York University, Conservation Center of the Institute of Fine Arts*.

———. 2008b. The effects of Butvar B-98 on bronze, MAC research project report, Queen's University, Kingston, Ontario.

Liau, L., T. Yang, and D. Viswanath. 1996. Degradation of PVB using TG/FTIR spectrometry. *Polymer Engineering and Science* 36 (21):2589-2600.

Monsanto Chemical Company. 1989. Butvar polyvinyl butyral resin: properties and uses. In *Coatings Performance Materials by Monsanto*. St.Louis: Monsanto.

Nakhla, S. M. 1986. A comparative study of resins for the consolidation of wooden objects. *Studies in Conservation* 21 (1):38-44.

Ng, W. 1992. Corrosion tests of copper coupons. (Unpublished report).

Paterakis, A. 1996. Conservation of a late Minoan basket from Crete. *Studies in Conservation* 41 (3):179-182.

Reinohl, V., J. Sedlar, and M. Navratil. 1981. Photo-oxidation of poly(vinylbutyral). *Polymer Photochemistry* 1:165-175.

Sakuno, T., and A. P. Schniewind. 1990. Adhesive qualities of consolidants for deteriorated wood. *Journal of the American Institute for Conservation* 29 (1):33-44.

Schniewind, A. P., and P. Y. Eastman. 1994. Consolidant distribution in deteriorated wood treated with soluble resins. *Journal of the American Institute for Conservation* 33 (3):247-255.

Spirydowicz, K. E., E. Simpson, R. A. Blanchette, A. P. Schniewind, M. K. Toutloff, and A. Murray. 2001. Alvar and Butvar: The use of polyvinyl acetal resins for the treatment of the wooden artifacts from Gordion, Turkey. *Journal of the American Institute for Conservation* 40 (1):43-57.

Toutloff, M. K. 1999. The effect of intense environmental conditions on Butvar B-98, MAC research project report, Queen's University, Kingston, Ontario.

Wang, Y., and A. P. Schniewind. 1985. Consolidation of deteriorated wood with soluble resins. *Journal of the American Institute for Conservation* 24 (2):77-91.