

## POLYMER SCIENCE & GUITAR STRINGS: KEEPING THE MUSIC ALIVE WITH SURFACE CHEMISTRY

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### Introduction

Musical instrument strings have benefited from a 100-year progression of improvements ranging from the use of synthetic polymer fibers<sup>1</sup> and protective coatings,<sup>2,3,4</sup> to the use of chemical surface treatments<sup>5</sup> and galvanically matched corrosion-proof materials<sup>6</sup> - all for the purpose of increasing longevity. Unfortunately, a major disadvantage of these strings was and still continues to be corrosion. In an attempt to "keep the music alive with surface chemistry," the present study was undertaken for the purpose of improving the corrosion resistance of phosphor bronze wound musical instrument strings. Two polymeric film-forming materials were evaluated for this purpose: benzotriazole (BTA), and N-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPS).

### Experimental

**Materials and Procedures for Corrosion Testing.** The musical instrument strings for this study included three types of commercially available constructions that were designed for acoustic guitar: phosphor bronze wound titanium-core strings from a set of Rohrbacher Low-Tension Titanium Acoustic Guitar Strings™; and two types of phosphor bronze wound steel-core strings - one from a set of John Pearse™ medium-tension acoustic guitar strings, and the second from a set of DR-Rare-Bronze™ light-tension acoustic guitar strings. All of the strings were used as received.

In each corrosion experiment, 30 ml glass vials with lids were filled with 5 g of a saturated aqueous NaCl stock solution (prepared with deionized water, and reagent grade NaCl from Aldrich Chemical). The string samples were cut into 1-1/4 inch strips, and were placed into the glass vials with a portion of each submerged below the water line, and with a portion of each above the air/water interface. Two visual criteria were used to qualitatively rank corrosion: the degree of winding discoloration above the water line, and the degree of turbidity below the water line.

In the first series of surface treatment experiments, the corrosion resistance of phosphor bronze wound strings was determined as a function of the relative coating weight of benzotriazole (BTA, Aldrich Chemical). The strings for this comparison included a John Pearse™ brand medium-tension "E" string (phosphor bronze wound steel core); and a Rohrbacher Technologies brand low-tension "E" string (C521 phosphor bronze wound Ti alloy core). Both types of strings were surface treated by dipping into various solutions of benzotriazole dissolved in a 95/5 weight percent mixture of denatured ethanol (Aldrich Chemical) and deionized water. Each wound section was separately dipped into a solution for one minute, and was then removed to air dry for 15 hours. One sample of each string was also tested as received (with no treatment). The samples were qualitatively evaluated as described above, and were ranked (from low to high) according to the relative degree of turbidity after 30 hours of exposure.

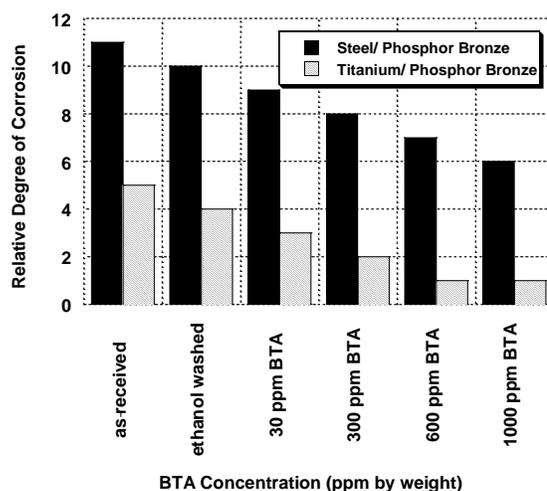
In the second series of surface treatment experiments, the corrosion resistance was determined as a function of the relative coating weight of AAPS. The strings for this comparison included a DR-Rare-Bronze™ brand light-tension "A" string (a C521 phosphor bronze wound steel core); and a Rohrbacher Technologies brand low-tension "A" string (a C521 phosphor bronze wound Ti alloy core). Both types of strings were cut as received into 1-1/4 inch strips as described above, and were then surface treated by dipping into solutions of pre-hydrolyzed AAPS, otherwise known as Z6020 from Dow Corning. The AAPS was prehydrolyzed by mixing 50 parts silane with 50 parts ethanol and 5 parts distilled water at 25°C. After 24 hours, the prehydrolyzed concentrate was diluted into 70/30 (v/v) isopropanol/water (Aldrich Chemical) to yield various solution concentrations ranging from 0.05% to 6.4% active silane by weight. Each wound section was separately dipped into a solution for one minute, and was then flash dried with a hot-air gun for a 2 second dwell time. The samples were then allowed to equilibrate under atmospheric conditions for 48 hours prior to corrosion testing.

Qualitative rankings were established based on the relative degrees of visual corrosion (as judged by turbidity), where the titanium-core sample with the lowest degree of corrosion (after 21 days of exposure) was ranked as 1, and the remainder of the group was ranked in sequence from low to high according to increasing degrees of turbidity. The steel-core samples (after 24 hours of exposure) were then ranked in comparison to this baseline, where the visual turbidity of the untreated steel-core control (after 24 hours of exposure) was noted to be equivalent in rank to the untreated titanium-core control sample (after 21 days of exposure). The other steel-core samples were then ranked in relative comparison to one another (from low to high) with respect to the titanium-core baseline.

**DMA Studies.** Dynamic Mechanical Analysis (DMA) was performed on DR-Rare Bronze™ brand light-tension "A" strings (untreated, and poly-AAPS treated). The analyses were performed on a TA Instruments model 983 DMA equipped with vertical clamps. The data were collected in resonant mode under ambient conditions using a sample length of 21 mm, and oscillation amplitude of 0.8 mm.

### Results and Discussion

**The Effect of BTA Concentration.** The qualitative corrosion results for BTA-treated steel-core and titanium-core strings are presented in Figure 1. The graph depicts the combined relative ranking (based on visual turbidity) of all of the solutions after 30 hours of exposure.



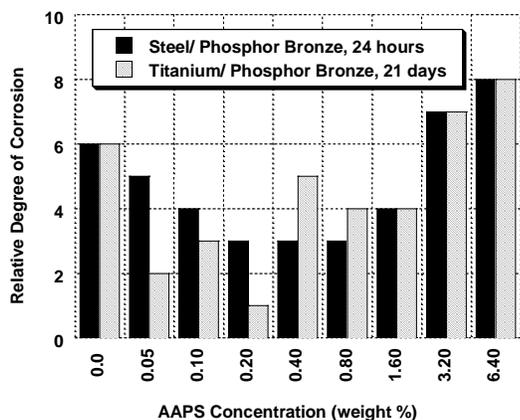
**Figure 1.** The effect of BTA surface treatment concentration (parts per million, ppm by weight) on the relative degree of corrosion of phosphor bronze wound steel-core and titanium-core strings.

The overall degree of corrosion among the titanium-core samples was significantly less than that of the steel-core samples, and the protection afforded by BTA was observed to increase monotonically in both sets. The initial differences were apparent above the water line (from partial oxidation and discoloration of the phosphor bronze winding), and below the water line (from the turbidity due to the build-up of corrosion byproducts and precipitates). After 3 days, the differences in steel core samples were no longer discernable (due to extreme corrosion), whereas the differences among titanium core samples remained visible for more than 1 week.

The corrosion inhibiting function of benzotriazole and other azole compounds is known to result from the ability of the azole functionality to chelate with the metal oxide surface to form an oxide-reinforcing polymer network, which provides protection against cathodic induced oxidation.<sup>7</sup> This is consistent with the finding that BTA lessens the oxidation of phosphor bronze when it is wound around a more cathodic titanium alloy core.

Similarly, BTA also provides anodic protection in cases where copper alloys are in contact with more anodic metals.<sup>7</sup> This is consistent with the finding that BTA lessens the oxidation of the more anodic steel core when it is wound with phosphor bronze.

**The Effect of Poly (AAPS) Organosilane.** Figure 2 provides a qualitative visual ranking of the relative degree of corrosion for both AAPS treated steel-core and titanium-core strings as a function of the silane surface treatment concentration.



**Figure 2.** The effect of AAPS surface treatment concentration (% by weight) on the relative degree of corrosion of phosphor bronze wound steel-core and titanium-core strings.

For the case of steel-core strings, the NaCl solutions were orange in color (due to the likely formation of  $\text{Fe}_2\text{O}_3$  precipitates), whereas the solutions for the titanium-core strings were blue in color (due to the likely formation of copper (II) precipitates). Although the trends in both sets were similar, the differences among the steel-core strings were discernable within 24 hours of exposure, whereas the differences among titanium-core samples could not be discerned for several days.

These results show that the corrosion resistance improves with increasing surface treatment concentration up to a level of about 0.2% poly (AAPS) by weight. Beyond this level, the degree of corrosion appears to become worse. Thus, up to a certain threshold level of surface treatment, poly (AAPS) appears to stabilize the surface of phosphor bronze against both cathodic and anodic reactions. Beyond this threshold, little to no visible corrosion protection is provided.

Given that poly (AAPS) improves the corrosion resistance of phosphor bronze wound strings, it appears that AAPS (like BTA) has the ability to stabilize the metal oxide surface layer. Given that Cu and its oxides are known to bind with BTA to form polymeric complexes,<sup>7,8</sup> it follows that Cu may also bind with the amine groups of polymeric AAPS. In fact, AAPS has been observed to complex with  $\text{Cu}^{2+}$  ions in other applications.<sup>9,10</sup>

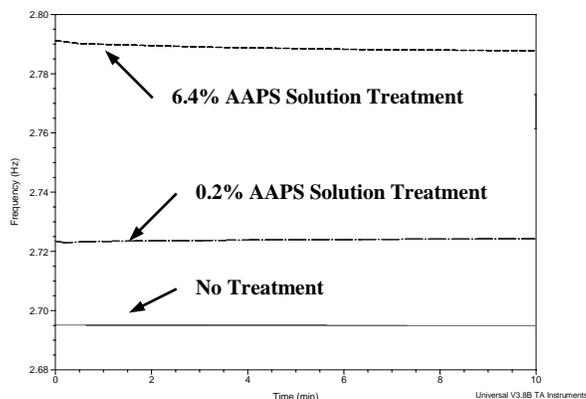
**DMA Studies of Poly (AAPS) Coated Phosphor Bronze Wound Strings.** DMA studies indicate that the mechanical properties of the strings are strongly influenced by the presence of the poly (AAPS) coating. Figure 3 shows that the coated strings resonate at higher frequencies, and that the relative stiffness increases in proportion with the weight of the coating. From the design standpoint, it is important to minimize these mechanical effects, especially since any change in mechanical properties can dramatically influence the acoustic characteristics of the string.<sup>4,6,11</sup> Fortunately, the results of this study show that the mechanical effects can be minimized, and that the corrosion protection can be simultaneously maximized through the use of lower coating weights.

## Conclusions

The present study suggests that poly (AAPS) has the capacity to provide corrosion protection to copper alloys; but only below a certain critical surface concentration. Specifically, it appears that like BTA, poly (AAPS) has the ability to stabilize the protective oxide layer on the surface of a phosphor bronze alloy under both anodic and cathodic conditions (as simulated by steel-

core and titanium-core musical instrument strings, respectively). Further extrapolation of these analogies leads to the suggestion that both compounds may provide corrosion protection through analogous mechanisms (i.e., through a combination of surface chelation and polymerization). Spectroscopic studies are currently underway for the purpose of studying these possibilities.

Thus, short of creating a "corrosion proof" string (i.e., a string constructed with galvanically matched materials like nickel and titanium<sup>6</sup>), a poly (AAPS) or BTA surface-treated string could be the next best thing - especially when the string is constructed with a titanium alloy core.



**Figure 3.** Resonant mode DMA (frequency vs. time) for a 6.4% AAPS treated steel-core string, a 0.2% AAPS treated steel-core string, and an untreated steel-core string.

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*Note: This technology has been used to develop "Silsesquioxane" Surface-Treated Steel-Core Acoustic Guitar Strings as well as Surface-Treated Titanium Acoustic Guitar Strings. Parker, A. A., "Organosilane Surface Treated Musical Instrument Strings and Method of Making the Same," U. S. Patent 7,476,791, January 13, 2009.*