INVESTIGATION OF A CURIOUS DISCOLORATION ON EXHIBIT CASE FABRIC

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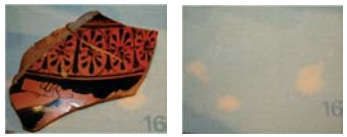
Figure 1: Kylix shard depicting a youth and volute krater (Attic red-figure, ca. 500 BC, Painter of London E2; MCCM 2003.60.5) and discolored spots corresponding to contact points on the display case fabric.

ABSTRACT

A curious discoloration was observed on the fabric beneath individual ceramic objects displayed in the Greek and Roman galleries at the Michael C. Carlos Museum of Emory University in Atlanta, Georgia. The discoloration was first noted several years ago when certain shards were repositioned, revealing the pinkish orange spots beneath points of contact with the case fabric. This discoloration was not seen beneath all ceramics, and the objects associated with discolored areas did not share ancient provenance or recent collection history. Treatment of the ceramics before they entered the Carlos Museum collection seemed a probable cause for the discoloration, but treatment records were not available. Spot tests with several cleaning agents used in recent decades by collectors, archaeologists, dealers, restorers, and conservators indicated that a similar discoloration of the fabric could be produced with hydrochloric acid. This preliminary observation suggested that the discoloration was due to the presence of residual chloride ions from prior treatment with hydrochloric acid. An ancient shard associated with the discolored case fabric was soaked in distilled water, and the bath tested positive for chloride ions through a reaction with silver nitrate. In an effort to replicate the discoloration, samples of case fabric were also exposed at elevated temperature and relative humidity to volatile hydrochloric acid from solvent solutions and from fragments of treated ceramics. This experimental design was modeled upon a version of the Oddy Test. This series of tests illustrates that hydrochloric acid used in treatment may not be completely removed from porous substrates. It is not known whether the previously treated ceramic shards were rinsed, as is often described in procedural descriptions, or if the cleaning agent was expected to volatilize, as is sometimes suggested. Exhibition and storage materials such as fabric, wood, carpet, paint, and plastic are routinely tested for the threat they may pose toward objects, yet in this example it is the collection objects themselves that provide a source for potentially damaging compounds.

1. OBSERVATIONS

A curious discoloration was observed on the fabric beneath certain ceramic objects displayed in the Greek and Roman galleries at the Michael C. Carlos Museum of Emory University (Figure 1). The grey fabric was discolored to a pinkish orange color where it had been in direct contact with some Classical ceramics, including both shards and complete vessels. The orange color appeared to be a color change rather than a stain. The discoloration also appeared where the ceramics did not make direct contact with the fabric-wrapped deck, but where air circulation was restricted as within the hollow under a vase foot. The discoloration was most intense where there had been direct contact between the ceramic and the fabric for an extended period. The objects associated with discolored areas were made in different regions at varying dates, and they were acquired from several collectors at separate intervals. None of the ceramics were treated at the Carlos Museum prior to exhibition.



Figures 2 & 3: Amphora shard depicting Herakles (Attic red-figure, ca. 470 BC, MCCM 2002.43.32a) and the discolored spots on the display case fabric beneath the shard.

The Greek and Roman galleries were reinstalled in early Fall 2004. The built-in cabinet cases where the discoloration is seen are not sealed and have been opened repeatedly since installation. The discoloration was first noted several years ago when a few shards were repositioned, revealing the pinkish orange spots beneath points of contact with the deck fabric (Figures 2 & 3). The fabric covering the case decks and risers is a plain-weave cotton fabric of unknown manufacturer. This fabric passed an Oddy Test performed at the time of purchase. It is presumed that the fabric was washed before use, as is routine practice to remove manufacturing finishes and residues. The decks and risers are wood constructions and were sealed with water-borne polyurethane and/ or Marvelseal prior to wrapping with the display fabric.

2. HYPOTHESIS

Previous treatment of the ceramics seemed a probable cause for the discoloration. None of the ceramics had been treated at the Carlos Museum, and there are no records of old treatments in the accession files. A few "typical" chemicals were selected from the numerous and varied cleaning solutions used in recent decades by collectors, archaeologists, dealers, restorers, and conservators. Spot tests were performed directly on a sample of the grey fabric using the following chemicals:

Hydrochloric acid [38%]
Sodium Hydroxide [50%]
Ammonium Hydroxide [28%]
Hydrogen Peroxide [30%]
Triethanolamine (TEA) [100%]

Each chemical was applied as a concentrated solution, and a single drop was applied to swatches of the grey case fabric and allowed to sit overnight. The treated swatches were observed during spot testing and after air drying to evaluate any visible change. High surface tension and slow wetting suggested the presence of a finish on the test fabric, which was cut from the unwashed stock bolt. The hydrochloric acid produced a pinkish orange color that diffused beyond the spot location and appeared similar to the discoloration seen in the display cases. The hydrogen peroxide caused a white discoloration that was isolated to the spot location (Figure 4). The other chemicals tested produced no visible changes in color.

Figure 4: Spot tests with concentrated hydrochloric acid (left) and hydrogen peroxide (right) applied directly to unwashed display case fabric.

Based on the results of these spot tests, it was hypothesized that the discoloration of the fabric was due to the presence of residual chloride ions from a prior treatment with hydrochloric acid. It was further hypothesized that at room temperature, the reaction of residual hydrogen chloride with approximately 50% relative humidity in the room, produces hydrochloric acid. To describe this reaction, the following equation was proposed:

$$HCl_{(v)} + H_2O_{(v)} \xrightarrow{(@\ rt)} H_3O^+ + Cl^-_{(s)}$$

Residual Hydrogen Chloride + 50% atmospheric vapor ⟶ Hydrochloric Acid

An unattached shard belonging to one of the objects associated with the discolored case fabric was located in storage. This shard was bathed to determine the presence of chlorides. This shard was soaked in 150ml of distilled water for approximately one week. The bath water was tested for chloride ions using a 1% solution of silver nitrate. A white precipitate formed, indicating the presence of chloride ions (Figure 5).

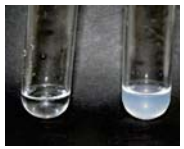


Figure 5: Chloride ion test with silver nitrate solution, showing a negative reaction with the distilled water control (left) and a positive reaction with the shard soaking bath (right).

The soaking bath was changed weekly for four weeks. The pH and conductivity of the bath water were periodically measured. During the first days of the initial soak, the bath water became slightly more acidic and the conductivity increased significantly. The pH and conductivity gradually reduced with each subsequent soaking bath. After four weekly changes of the soaking bath, the pH reached neutral and the conductivity was 49µS (Figure 6). A silver nitrate test performed on the final bath did not produce a positive reaction for chloride ions.

Both the spot tests and the presence of chloride ions in soaking bath suggest that prior treatment with hydrochloric acid might be the cause of the pinkish orange discoloration on the case fabric.

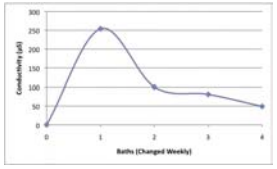


Figure 6: Graph of conductivity measurements from four successive shard soaking baths.

3. EXPERIMENTAL

A brief literature survey revealed that treatments with hydrochloric acid generally involve solutions ranging in concentration from 2% to 20%. Treated ceramics were brushed repeatedly with the cleaning solution or were soaked for a period of time. Most procedures described a preliminary soak in distilled water and a final rinse in distilled water. None of the treatments described a method to evaluate whether the hydrochloric acid cleaning solution had been thoroughly rinsed away. Some discussions seemed to imply that the residual cleaning solution would volatilize. Treatments with hydrogen peroxide were frequently referenced, so this cleaning method remained of interest in the evaluation of possible discoloring agents.

Two experimental scenarios were intended to induce discoloration on the case fabric by (1) indirect exposure to hydrochloric acid or hydrogen peroxide cleaning solutions and (2) contact with treated ceramics. In each scenario, the case fabric was subjected to elevated temperature and relative humidity in an experimental set-up modeled upon the version of the Oddy test described by Bamberger, et al. Fourteen glass jars with plastic lids were prepared with 1ml of distilled water. A small beaker was placed inside each glass jar.

Measured 1ml volumes of six cleaning solutions (hydrochloric acid or hydrogen peroxide at concentrations of 2%, 10%, and 20%) were each put into beakers within separate jars. A seventh beaker with 1ml of distilled water was prepared as a control. Strips were cut from a washed sheet of the case fabric and creased in thirds to correspond to the width of the small beakers. These strips were placed over the mouth of each beaker, and the glass jars were sealed with silicone grease (Figure 7).

Figure 7: Experimental set-up for indirect exposure of fabric strips to hydrochloric acid or hydrogen peroxide cleaning solutions.

Figure 8: Experimental set-up for exposure of fabric strips by contact with treated fragments of a ceramic flowerpot.

A second set of fabric strips was placed in contact with newly treated test fragments. In order to replicate the treatment that the ancient ceramics may have received, fragments of an unglazed ceramic flowerpot were treated with one of the six cleaning solutions of hydrochloric acid or hydrogen peroxide at 2%, 10%, or 20%. The flower pot fragments were first saturated with distilled water and then soaked for three hours in one of the solutions. An unsoaked fragment served as the control. Strips of pre-washed fabric were placed inside seven small beakers, and one of the flowerpot fragments was placed directly on the fabric. The glass jars were then sealed with silicone grease (Figure 8).

The fourteen jars were placed inside a Pyrex dish, put into a lab oven, and held at approximately 60°C for four weeks.

4. RESULTS

The jars were monitored weekly by inspection through the glass walls; the jars were not opened. After the first week, a color change was observed on the fabric strips enclosed with the 20% solutions of hydrochloric acid and hydrogen peroxide. After two weeks, the water in some jars had become brown and condensation was present on the walls of some jars.

The seven jars containing beakers of cleaning solutions were removed from the oven after three weeks. All of the exposed fabric strips showed color changes. The strips exposed to hydrogen peroxide solutions were discolored to: somewhat orange (2%), white (10%), and beige (20%). The strips exposed to hydrochloric acid solutions were discolored to: pale orange (2%), pale pink (10%) and white (20%). The fabric exposed to 20% hydrochloric acid solution became brittle, breaking along a crease and at the edges (Figure 9).

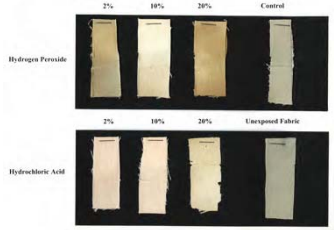


Figure 9: Strips of fabric exposed to cleaning solutions for four weeks at 60°C.

The jars containing the treated flowerpot fragments were removed from the oven after six weeks. A slight color change was visible on the fabric strip that had been in contact with the flowerpot fragment treated with 20% hydrochloric acid (Figure 10 & 11).

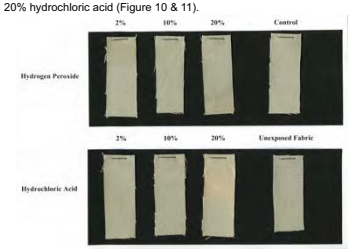


Figure 10: Strips of fabric in contact with treated flowerpot fragments for six weeks at 60°C.

Figure 11: Strips of fabric in contact for six weeks with a flowerpot fragments that had been treated with 20% hydrochloric acid solution (left) and an untreated fragment (right).

5. CONCLUSIONS

This investigation suggests that the case fabric is being discolored by contact with ancient shards that were previously treated with hydrochloric acid. The discoloration was reproduced through a spot test with hydrochloric acid applied directly to the case fabric. Residual chloride ions were extracted from an ancient shard associated with the discoloration by repeated soaking in baths of distilled water. A reaction with silver nitrate confirmed the presence of chloride ions; conductivity and pH measurements illustrated the loss of chloride ions through repeated bathing. Discoloration was also induced on samples of case fabric that were exposed at elevated temperature and relative humidity to volatile hydrochloric acid from solvent solutions and from newly treated ceramic fragments. Each of these tests and experiments supports the hypothesis that the discoloration seen on the fabric could be caused by hydrochloric acid migrating from the ancient ceramic shards while on display.

The effects of previous treatments are often visible on the objects themselves, but in this example the damaging effect manifested on the adjacent display fabric. The presence of volatile organic compounds such as hydrochloric acid can have harmful effects on a variety of museum objects, in particular metals and organic colorants. While exhibition and storage materials such as fabric, wood, carpet, paint, and plastic are routinely tested for their potential to damage objects, in this example the possible threat is posed by the objects themselves.

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