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Compiled by Virginia Greene and Patricia Griffin

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FOREWORD

This is the 9th volume of *Postprints* published by the Objects Specialty Group (OSG). It includes a selection of papers originally presented at the OSG Session, June 10, 2001 as part of the American Institute for Conservation (AIC) Annual Meeting in Miami, FL. The day was divided into morning and afternoon sessions that focused on two diverse themes of wide interest to objects conservators.

The theme for the morning session- Considerations of Surface and Aesthetics in the Treatment of Outdoor Sculpture and Monuments- was designed to provide a venue for the presentation of current hands-on practices in the conservation of outdoor sculpture. Papers included treatment case studies that discussed the original aesthetics, and/or the thought processes that informed the aesthetic choices made during treatment; as well as the evaluation of materials or techniques used for cleaning, patination, coating, and painting. There was also a lunchtime discussion after the session that was informative and dynamic. Despite a historic awareness of their changing condition, and their long history of conservation intervention; there remains a body of diverse practices and opinions regarding the treatment of outdoor sculpture, with many avenues for future thought and study. Four papers from this session appear in this volume. Tara J. Shedlosky, Kimberly M. Stanek and Gorden Bierwagen present an overview of a survey on current practices in outdoor bronze conservation, with recommendations for future research. Two papers by Paul S. Storch and W. T. Chase describe the treatment protocols and re-evaluation of past treatments. Finally, Michael Belman presents three case studies in which ethical considerations strongly influenced the decision-making process. It is unfortunate that so few papers from this session made it to press; we hope that the other presenters will find the time to shape their research and ideas into a publication for another venue.

The theme for the afternoon session - *The Conservator as Connoisseur, Scholar, Detective* - was designed to illustrate the ways that conservators make important contributions to the body of information available towards the study of art objects; augmenting the disciplines of art history, archaeology, material culture and/or museum studies. These contributions can be developed through careful looking (conservation connoisseurship), technical study and/or treatment. Happily nearly all of the presenters from this session contributed - six papers in total. In two papers, Jane Bassett and Laramie Hickey-Friedman demonstrate that a careful cataloguing of condition and technological features provides critical evidence towards establishing provenance and authenticity. Paul Benson and Robert S. Gilmore discuss acoustical microscopy, a new and potentially useful examination technique for documenting hallmarks on gold and silver; because it images the deformation of the metal by below the surface left by tooling, this technique may also aid the study of archaeological metals that were formed and decorated with coldworking techniques. Stephen P. Koob illustrates the way that treatment, careful examination and conservation connoisseurship towards both the successful treatment and correct interpretation of archaeological glass fragments. In their papers, John Hirx and Samantha

Alderson contribute to our knowledge of the materials and technologies of ceramic production for two different and important cultural centers.

This volume also contains two papers originally presented at the Research and Technical Studies (RATS) Session, June 8, 2001 at the AIC meeting in Miami, FL. John Hirx and Michele Derrick organized the session and Virginia Greene solicited the papers for inclusion in this volume. Laramie Hickey-Friedman presents a review of the correct techniques and interpretation of ultraviolet light examination. Steven Weintraub provides an overview of the types and proper usage of silica gel.

On behalf of the OSG, I thank everyone that participated in the session. To Virginia Greene, I extend deep and heartfelt thanks for her enduring and excellent work as the *Postprints* editor. She has assumed this responsibility since 1995, and the written body of knowledge that has resulted is a testament to her exemplary professionalism. All of the presenters at the two OSG sessions made valuable contributions. Collectively, they showed a great range of problems and subject matter; demonstrating the considerable research, thought and problem solving that goes hand in hand with our profession. However, those that contributed to this volume have made an indelible contribution. Publication is a permanent way to share our hard-earned knowledge and insights. Publication is vital to the continued development of our profession-- especially now, as it is the common thread linking our goals of public outreach, certification and professional development.

Pat Griffin, OSG Chair 2002-2003

ON-LINE SURVEY RESULTS OF TECHNIQUES USED FOR OUTDOOR BRONZE CONSERVATION

Tara J. Shedlosky, Kimberly M. Stanek and Gordon Bierwagen

1. Introduction

A survey on the methods and materials used by outdoor bronze conservators was conducted to obtain a broad opinion of both practical information about the techniques and materials used to maintain outdoor sculptures and the future needs of the conservation community relating to coatings for outdoor bronze sculpture. Through this survey we hoped to develop specifications for formulating coatings for outdoor bronze which the authors of this paper will attempt to apply to novel coating ideas for outdoor bronze conservation.

The survey was conducted on-line to insure anonymity in the responses, as some of the questions could be interpreted as ethically challenging. The cost of addressing people on line was a more efficient use of time and funds verses sending out mass mailings to conservators. In addition, contacting people on-line allowed to easily communicate with conservators throughout the world.

A letter in the form of an e-mail was sent out to approximately 500 conservators including: sculpture conservators from the AIC Directory, people who participated in the Metals 2001 Conference and people on the Conservation On-line Distribution List (CoOL) who listed themselves as working with bronze. In addition a request was posted on CoOL. The letter included a password to enter the on-line survey to ensure only the targeted conservators would be able to fill out the survey. The entered data was stored on a controlled spreadsheet. This made the process efficient, avoiding having to reenter the results.

A total of 38 people answered the survey. Although this seems like a low percentage of participants, the following statistic indicate that those who did respond are very important to the preservation of bronze objects. Of these responders, 95% had cleaned, 87% had coated and 58% had repatinated an outdoor bronze. These statistics indicate that the people responding to the survey have relevant backgrounds that represent true practices of outdoor bronze conservation and maintenance. Throughout the remainder of this paper, these respondents will be referred to as the "conservators".

2. Survey Results

2.1 Cleaning

When asked about the materials used to clean outdoor bronze, 40% of the respondents use nylon

brushes or scrub pads and 51% use natural brushes. The following chart represents the different detergents reportedly used by conservators and the percentage of conservators that report using each detergent.



Figure 1. Different types of detergents used by conservators

Triton-XTM (a registered trademark formerly owned by Rohm and Haas Co., but now owned by Union Carbide) is a nonionic detergent. The "X" series of Triton detergents are produced from octylphenol polymerized with ethylene oxide. Orvus[®] WA Paste is produced by Proctor and Gamble it is reportedly an extremely gentle detergent designed to clean cattle and horses. In the "other" category detergents that are used are Vulpex, Teric 90, and the surfactant Synperonic N. Ivory[®] dish detergent was also reportedly used.

Blasting is sometime used to remove unwanted films and clean items. It was reported that 44 % of the conservators had used this technique to clean a bronze sculpture about 1.5 % of the time. The following graph represents the different materials used to blast sculptures and the number of conservators reportedly using them.



Figure 2. Blasting Media used to clean bronze sculptures.

2.2 Coatings

Atmospheric corrosion is becoming more prevalent throughout the world and results from an increasing production of corrodants such as SO_x , NO_x , CO_2 , and chlorides. These corrodants affect various materials including bronze. Unprotected outdoor bronze corrodes readily when an electrolyte comes in contact with the metal. The metal, acting as the anode, readily oxidizes while a cathodic reduction reaction of O_2 and H_2O occurs. Protection from bronze corrosion is thus very important when trying to conserve bronze sculpture situated in a hostile environment. In attempting to maintain the original intent of the artist one must protect the bronze with the least intrusive means possible. The primary method of protecting bronze from elements found outdoors is using a protective coating. In developing a protective coating it is important to understand what is wanted and needed by the conservation community.

The surveyed conservators were asked to rate various potential properties of a coating on a sliding scale and report where the feature lay between very important and not important. The following figure graphically represents the results.





The above results indicate that the three most significant features to build into a coating are weather resistance, the appearance of a coating on a bronze and the ability of a coating to be removable. The three other features as well are indicated as important to a majority of the surveyed. It was pointed out in the comments section of the survey that cost and availability of the coating system are issues that also must be addressed.

2.2.1 Wax

Wax is by far the most popular coating system used on outdoor bronzes. Wax is assumed to be protective, and fully removable. Although comments from a surveyed conservator say, "... wax can build up and change the appearance from multi-colored to a thick and glossy uniform brown. Further, it is very difficult to remove a wax coating and raised areas of bronze on the surface still become worn down and turn green. The wax can also assist harmful materials such as stray fertilizer pellets, in damaging the surface of the bronze by eating through via small openings and spreading under the layers of wax." Nevertheless, wax is a cost effective material and is easily applied and thus readily used. This same conservator went on to say that, "most curators and museum visitors, etc. aren't bothered by the change in appearance. Like so many (preventive) conservation treatments, protective wax coatings seem more beneficial than most other coatings at this time." The survey results indicate the popularity of wax, as 92% of the surveyed conservators have applied wax coatings. Brushing and cloth applications of wax are the most popular; only 9% had used spraying methods to apply the wax. Application of a hot wax technique was used by 62% of the surveyed and 70% of conservators have tinted the wax. The graph below in Fig. 4 represents the average wax reapplication.



Figure 4. Average wax reapplication.

Typically wax is applied once per year. It was pointed out by a conservator that, "postconservation maintenance of outdoor sculpture is often the responsibility of the institutional owner" and therefore out of control of the conservator. The following figure graphically represents the types of waxes and their frequency of use by conservators.



Figure 5. Types of Waxes and frequency of use.

Butcher's bowling-alley-paste wax, which is a carnauba wax, natural and synthetic waxes in mineral spirits and turpentine (or other hydrocarbon), is the most popular type of wax (Scott 2002). The microcrystalline blends are also commonly used and are often mixed by the conservator. Other waxes that were reported to be used are carnauba blends and synthetic beeswax. It was reported that Renaissance Wax was not used at all outdoors.

2.2.2 Pretreatments

Corrosion inhibitors retard the formation of corrosion through complex mechanisms, which are often more than simple barrier properties. The inhibitors suppress either the cathodic or anodic or both electrochemical reactions. In the case of benzotriazole (BTA), the molecule is chemisorbed on the metal substrate. This chemisorption is facilitated by the polar nitrogen molecules (Jones 1996). A total of 57 % of the surveyed conservators, have used a corrosion inhibitor, all report the corrosion inhibitor used as BTA. BTA pretreatments were used under both wax and non-wax coatings.

2.2.3 Non-wax Coatings

Synthetic resins are used to protect bronze instead of using a wax coating. The conservators report that 73% have used a non-wax coating. 90% of the conservators would find it valuable to be able to adjust the gloss of the system. The following figure represents the different coatings that are used and number of conservators who use each.



Figure 6. Types of resins that are used on outdoor bronze.

Incralac[®] is the most popular resin used to protect outdoor bronzes. Incralac[®] is an acrylic polymer-based coating that is soluble in toluene. Incralac[®] was developed in the 1960s by the International Copper Research and Development Corporation in New York (Scott 2002). The base of Incralac[®] is the resin Paraloid B-44 made by Rohm and Hass Inc, which is a ethyl methacrylate/methyl methacrylate copolymer. In addition to Paraloid B-44, Incralac[®] contains a leveling agent, epoxidized soybean oil, an ultraviolet stabilizer – benzotriazole (BTA), toluene and ethanol. BTA also functions as a corrosion inhibitor for the copper in the bronze and is present in the formulation. There have been several studies that have looked at the effectiveness of Incralac[®] and the conclusions of these studies indicate that Incralac[®] is an effective coating varying from 16 months to 5 years of outdoor exposure (Scott 2002; Weil 1980; Smith and Beale 1986; Brostoff et. al. 1998; Brostoff and de la Rie 1997; Bierwagen et. al. 1999). Thus every 2-5 years efforts must be made to remove the old coating system and then reapply a new coating. Minimizing this step of removing and then reapplying a new coating can be achieved by finding a better coating system to replace Incralac[®].

2.2.4 New Coating Systems

The conservation community on a whole agrees that research needs to be continued to develop polymer coatings for the protection of outdoor bronze sculptures (Scott 2002). In attempting to develop a coating for outdoor sculpture, it is important to the authors to understand what type of coating would be accepted by the conservation community. The following statements refer to a fictional coating that would perform better than what is currently available. If a protective clear coating was developed and it was not removable by solvents, 29% of the surveyed conservators would use it. If the same coat was removable by mechanical means 31% would use it. If the means did not change the surface 63% would use it. If a different method was developed for removing the coating without changing the surface, 87% would use the coating. When asked about the need for a long term coating system, which was defined as longer that one year, 92% said there was a need for a long-term coating system. Fig. 7 represents the lifetime specifications for a model coating system as defined by the conservators.



Figure 7. Lifetime Specifications for a model coating system as dictated by the surveyed conservators.

There seems to be a need for a long term protective system, especially if it is removable by a novel technique that does not disturb the surface. There was some concern that if a long term coating system were developed, annual inspections would not be upheld by the owners of the bronze.

The following represents the coating specifications of an *ideal* coating system, as defined by the survey questions and the comments that were submitted to the survey. The coatings must have the following characteristics:

• Protective against corrosion formation (provides a barrier against water, O2, or ions)

- Clear (must be able to conform to the optical properties as the conservator and curators sees fit, gloss adjustable)
- Removable
- Easy to apply
- Non-toxic (as little as possible)
- Durable
- Not Degraded by ultra violet light
- Cost effective

3. Current Research

This research was recently reported at the 2002 Athens Conference on Coating Science and Technology (Bierwagen et. al. 2002). For a more in-depth analysis, please refer to the references.

A fluoropolymer is being studied as a protective coating on bronze when blended with an acrylic polymer. The acrylic used is Paraloid B-44, which is an acrylic resin made by Rohm and Haas. This acrylic also happens to be the base for Incralac[®]. We are currently studying another Rohm and Haas acrylic, Paraloid A-21, in hopes of furthering the adhesion of the fluorocarbon.

Electrochemical methods such as electrochemical impedance spectroscopy are techniques that provide a quantitative analysis of a corroding material (Bierwagen et. al. 1996; Wain et. al. 1996). Electro-chemical impedance spectroscopy (EIS) is one of the electrochemical methods that can be utilized to characterize the corrosion protection of coatings (Jones 1996; Skerry and Eden 1987; Bierwagen 1996). As the corrosion protection of the coating decreases so does the impedance. An increased amount of electrolyte penetrating into the coating is indicative of poor corrosion protection and increases the capacitance of the system. The capacitance increase shows its effects in the higher frequency portions of the EIS spectrum, but at low frequencies is identified with an increase in water uptake in the film and a decrease in film resistance.

EIS analysis of the protective coatings on monumental bronze was determined by application of an alternating current of 5mV to the cell. The electrochemical cell consisted of a saturated calomel reference electrode and a platinum mesh counter electrode that were immersed in dilute Harrison electrolyte solution. The electrolyte stayed in contact with the working electrode sample by using an o-ring clamp with an area of 7.0 cm². A Gamry PC3 potentiostat with CMS 100 software was used to collect the data over the frequency range of 5000 to 0.1 Hz.

The following is a Bode Plot of various coatings on bronze before any weathering occurred.



Figure 8. Bode plot of various coatings on bronze, at time zero.

Initial electrochemical studies indicate that the fluorocarbon-acrylic blend has the potential of being an excellent coating. The following figure, measured initially after the coating was cast over the bronze substrate, demonstrates the initial electrochemical impedance spectroscopy (EIS) results of the blend on rolled bronze. It indicates the greater barrier properties of the fluoropolymer-based coatings. The low frequency portion of this Bode plot, indicate that the fluoropolymer-acrylic blend is highly resistant coating. The authors would like to note the significant difference in resistance between that of the wax and the resistance of the acrylic and acrylic blends at low frequencies, even before weathering has occurred. Further studies will again look at increasing the adhesion of the coating, along with artificial weathering of the coating on cast bronze.

4. Conclusions

Through this on-line survey, a general overview of materials and methods used in outdoor bronze conservation was obtained. It was found that there seems to be a need for a long term protective system, especially if it is removable by a novel technique that does not disturb the surface. Coating specifications were generated as a goal when developing an ideal coating system. Initial results indicate that there is potentially a significant area of growth in coating systems.

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TEN YEARS OF SCULPTURE AND MONUMENT CONSERVATION ON THE MINNESOTA STATE CAPITOL MALL

Paul S. Storch

"Art is, among other things, both the terrain of, and often a weapon in, the culture wars that course through societies. This is, of course, especially true of public art- the art chosen self-consciously by public institutions to symbolize the public order and to inculcate in its viewers appropriate attitudes toward that order. Although occasional museum curators may devote themselves to "art for art's sake", I think it fair to say that this concept makes no sense to anyone concerned with the art that is found in those spaces that are most truly "public" in a political sense, such as the space surrounding capitol buildings, city halls, national cemeteries, and the like." (Levinson 1998)

1. Introduction

This paper focuses on the organization, management, and methodologies developed over the course of a decade to deal with a diverse set of sculptures and monuments in a harsh Upper Midwestern climate. The Minnesota Historical Society (MHS) has had statutory and fiduciary responsibility for the sculpture and monuments on the 36 acre State Capitol Mall since the founding of the MHS in 1849 (Fig. 1). It has only been since the late 1980's that the various administrative agencies and entities in the state government have fully recognized and enabled this role by including the MHS as a full partner and advisor in the long-term care of these monuments.

As a by-product of managing and conserving the monuments in partnership with the Capitol Area Architectural Planning Board and the State Department of Administration Architect's Office, the author and other MHS conservators have participated in the conservation and maintenance of nine sculptures and monuments (Fig. 2). During this time, the *de facto* State Capitol Mall Sculpture Conservation Program was created. Products of this program include an emergency response plan, a treatment tracking document, a research paper, and two AIC presentations. The goal of this paper is to describe the evolution and structure of the conservation program, and to detail three applied research projects that have resulted from it.

A monument may consist of a traditional bronze portrait figure (Fig. 3), a fountain (Fig. 4) or a complex sculptural plaza assemblage (Fig. 5). As a by-product of these projects, three different sculpture conservation research projects with two different contracting conservation firms were completed between 1992 and 2002. These projects have also resulted in applied research in metal cleaning, coating testing, and gilding techniques and methods. See Appendix I for the list of sculptures and their current conditions. The table is used to track treatments and other actions taken on the sculptures and memorials.

2. Roles and Responsibilities

The technical aspects of the projects and program were done in the context of working within a large, complex bureaucracy. Conservation of the Mall monuments is a responsibility of the Minnesota Historical Society. There are, however, several other state agencies with oversight and fiduciary responsibilities. Problems and solutions in communications, coordination, and control were encountered and overcome. The MHS/Mall situation is possibly a unique one in that outdoor sculpture conservators usually are contracted to work on one monument at a time. In general, the staff of the contracting agency has no knowledge or experience with the technical aspects of art or sculpture conservation, nor do they contact anyone for help in developing the request for the proposals. As the program has progressed over time, we are now responsible for conserving and maintaining fourteen outdoor monument assemblages. Although it is beyond the scope of this discussion to go into details, suffice it to say that state politics and money allocations from the State legislature play a central role in determining what can be conserved and when. The coordination of the MHS with other agencies responsible for the physical plant of the Mall results in a positive pooling of resources and relevant expertise. The use of outside contractors for specific projects augments the staff of the MHS conservation department. Within the MHS, the Site Manager for the State Capitol acts as the general coordinator for each project. The Senior Objects Conservator writes and develops the technical specifications for the RFP (Request for Proposal) documents, and the MHS Contracting Officer develops the legal parts of the contracts. Occasionally, the State Historical Architect is brought in for advice on the technical aspects of project development. Once a vendor is chosen, the Site Manager, Senior Conservator, and MHS Art Curator meet and work with the vendor on-site. The Art Curator is involved in decisions on repairs, coloration, and other issues that may affect the aesthetics of the sculpture or monument. The MHS Conservation Department Head may also be involved in any given project as an overall conservation advisor. Once a project commences, the State Capitol Historic Site Manager and the Senior Objects Conservator work act as coordinators between the Vendor and Plant Management staff, insuring that the Vendor has the equipment and access to on-site utilities that the State agreed to provide. The Vendor may train State Plant Management staff in sculpture maintenance procedures if that was part of the contract. Once the sculpture is conserved, the Senior Objects Conservator works with Plant Management staff on routine maintenance procedures on an annual basis.

3. Actual Projects

3.1 Charles Brioschi, Statue of Christopher Columbus

The first project of the State Capitol Mall Sculpture Conservation Program was in 1991 with the donation of money from the Italian-American Society to the MHS for the conservation and preservation of the Christopher Columbus statue located on the northeast side of the Mall (Fig. 6). Sculpted of bronze by Charles Brioschi and dedicated in 1932, the statue had never been

properly maintained. It had weathered and corroded from its original "Roman bronze" patination to a dull, mottled greenish-tan. The Italian-American Society requested that the treatment be completed in time for the 500th Columbus Day anniversary celebration in October 1992. The project was submitted for bids from contract conservation firms, and Fine Objects Conservation Inc. (FOC, Inc.) was awarded the bid. Based on her work on the Garfield Memorial at the US Capitol, Linda Merck-Gould, president of FOC, Inc., proposed that the bronze be cleaned with medium pressure water (1000-1400 psi), followed by an application of benzotriazole, chemical patination, and coating with Incralac and carnauba wax. Ms. Merck-Gould devised an on-site testing project that would take place prior to the actual treatment of the sculpture in order to finalize the treatment specifications. The exact details and results of the testing done on the Columbus sculpture in coordination with the MHS conservation department were published in a paper presented by Ms. Merck-Gould at the 1993 ICOM Committee for Conservation Conference (Merck-Gould 1993) (Fig. 7).

The main advantages of the water pressure method over other blast methods are as follows:

- Patina application can be done with greater fineness and results in a more subtle patina (Fig.8).
- The bronze surface does not undergo any deformation, based on tests published by Andrew Lins in 1989 using 750 psi. Even "softer" abrasives such as walnut shells and corn cobs cause loss of surface metal (Lins 1992).
- The health hazard from inhalation of dust to the operator and passersby is eliminated.
- There is no expended abrasive to clean up around the site. This is especially a concern on the heavily trafficked Mall.
- The technique takes less time to perform than particulate abrasive techniques and is therefore less costly.
- The appearance of the bronze surface is very similar to that left by walnut shell cleaning, and does not leave a bright metal surface.

The main disadvantage is the required skill level of the operator who will be doing the actual water pressure cleaning.

The detailed tests on the self-base of the Columbus statue to determine which pressures higher than 1000 psi could be used (Fig. 9) included the following objective: to remove the soluble corrosion products from the surface and the pits in the bronze without removing metal. The test methods included pressurized water at 1000, 2000, 3000 and 4000 psi, in comparison with 10.5 AD walnut shell powder at 35 psi. All cleaning method tests were reviewed at 37.5x

magnification using an Olympus stereomicroscope and photo-documented with color slides and black and white film.

The technique that removed the soluble, active corrosion from the surface and pits of the bronze was 4000 psi using a 25 degree fan tip. The surface retained a light green corrosion layer and was not stripped to bright bronze.

The rest of the treatment was carried out and was successful in restoring the bronze to the 1932 appearance of Roman Bronzework brown (Merck-Gould 1993). Unfortunately, in October 1992 just prior to Columbus Day, the statue was attacked in the middle of the night by vandals who doused it with an oil-based red paint. An emergency cleaning effort early the next morning by the State Department of Administration Plant Management Division used an outside non-conservation-trained local contractor. The contractor removed the paint in time for the holiday, but damaged the wax and Incralac layer to the extent that it had to be chemically stripped and replaced in the summer of 1993, and the statue re-treated in 1994 (Fig. 10). Since then, yearly maintenance has preserved the patina and surface coatings in a satisfactory manner (Fig. 11). This incident called out the need to create a useable monument and sculpture disaster response plan so that everyone necessary could be called in if something like this occurred again. A copy of that plan can be found at the end of this article (Appendix II).

3.2 John Karl Daniels, Statue of Leif Erikson

In 1995, the Sons of Norway, a local benevolent society, having seen the success of the conservation of the Columbus statue, donated money to the state for the treatment of John Karl Daniels 1949 bronze statue of Leif Erikson. Again, Linda Merck-Gould's firm, now known as Conservation Technical Associates, LLC, was awarded the bid for the contract. The statue was treated with medium pressure water at 3800 psi. (Fig.12), chemically patinated, and coated with Incralac (Fig. 13). The innovation used in this treatment was developed by Joe Sembrat, who was working for CTA at that time. Joe had researched paint and coating industry thickness testing methods and how they could be applied to outdoor sculpture conservation treatments. A DeFelsko Corporation NSI Positector 6000 thickness tester was used to verify that the manufacturer recommended thickness of 1.0 mil +/- 0.1 mil for the Incralac coating was indeed obtained (Figs. 14 and 15). The electronic instrument operates on the Eddy Effect, which is used to gauge the distance of a magnetic coil probe to a non-metallic surface. As the probe is moved close to the object surface, the inductance decreases and the resistance increases, which allows the thickness of an intervening surface coating to be measured. The instrument is zeroed-out on an uncoated area, then a series of 10 readings are taken over the coated areas and averaged together. The instrument is accurate to ± -0.1 mil. The difficulty in using the instrument on such a heavily textured sculpture as this one is the problem of finding a large enough flat area for a precise reading. The self-base lends itself to such an instrument. The textured areas, however, have a large variance in the readings. This method was used to verify the coating quality at the time of

treatment, and has been used annually since then to measure the wear to the coating. The measurement locations were mapped on photographs of the sculpture to allow for reproducibility of the readings in subsequent years (Fig. 16). The thickness coating tester has been a valuable addition to the equipment of the sculpture program, and is now written in the specifications for all other outdoor treatment projects that involve coatings.

3.3 Daniel Chester French, Progress of the State (Quadriga)

A gilt copper sculpture was designed and installed by Daniel Chester French on the South side of the roof of the new capitol building in 1905. It is officially entitled Progress of the State, and is commonly called the Quadriga (Fig. 17). The sculpture is a monumental four-horse chariot with three large human figures. The assemblage was re-gilded in 1949 and 1979. By the early 1990's it was obvious that the sculpture and the portion of the roof to which it was mounted required immediate and substantial conservation. The original mount and roof configuration had been changed in 1949 or earlier, and these modifications had actually exacerbated weathering and corrosion. The author was heavily involved with the writing and development of the Request for Proposal (RFP) for the Quadriga Conservation Project from 1994 through the completion of the project in 1996, and served on the state committee that oversaw the contract process. The conservation contract was awarded to Linda Merck-Gould, Conservation Technical Associates, LLC (CTA). CTA removed the assemblage from the capitol roof and moved it to Connecticut for treatment. The treatment included structural repairs and modifications, re-gilding, and tinted waxing and was based on an extensive amount of primary source research in the New York Public Library and New York Historical Society collections of French's and Cass Gilbert's letters and records on the original methods and materials used. The research revealed that the sculpture was coated with tinted wax in 1905.

The sculpture was spot re-gilded under warranty during the summer of 1997, and routine maintenance was performed by the author and assistant. By 1999 it was noticed that spot corrosion was occurring on various areas of the chariot and on the undersides of the horses (Fig. 18). There was a concern that the most recent treatment had not properly removed all of the solvent used to soften the 1979 primer layer, which may have compromised the new gilding layers leading to water infiltration and corrosion formation. Another hypothesis was that the solvents in the wax were weakening the sizing and allowing for increased corrosion. In 2000 and 2001, after the required RFP process, a contract was awarded to Jensen Conservation Associates, Omaha, NE, to examine the problems and to propose a course of action. Two copper panels salvaged from the roof beneath the Quadriga were gilded and set up in a test rack in late 2001. Each panel was divided into quadrants. One quadrant was left uncoated as a control, and the other three were protected with various combinations of waxes, pigments, and lacquers (Fig. 19). By the Spring of 2002, the test panels indicated that the type of weathering and wear that was seen on the Quadriga is a natural result of the conditions to which the surface is exposed, rather than an effect of workmanship or material from a previous treatment. The waxes and lacquers did not enhance

corrosion on the test panels. The rack will be left in place as a control and reference to track ongoing weathering effects on the Quadriga.

The normal life-span of a gilt sculpture in a temperate climate is approximately 20 years. The observations and research done as part of the sculpture conservation and maintenance program show that the failure of the gilt layers is progressive over that period and may proceed at different rates depending on the location of the surface in terms of environmental exposure and moisture condensation. From a fiscal management perspective, the decision was made to spot treat each of the corroded areas at this time and to continue the annual maintenance regime of washing and rewaxing (Fig. 20). Spot re-treatment, which includes removal of the corrosion (Fig. 21), and regilding (Figs. 22, 23) is a more efficient use of funds and will extend the life-span of the surface layers over the long term. Cleaning and re-waxing, while effective to an extent, will not prevent the need for re-gilding at some point. Incremental regilding, along with the stabilization and repair of failed joins, for example, will maintain both the structural and aesthetic aspects of the Quadriga.

4. Conclusion

Having an institution such as the MHS involved with the conservation management of outdoor sculptures and memorials has been greatly beneficial to the care and preservation of those objects. When state agencies, or other governmental entities such as city parks departments, attempt to "clean" sculptures either in-house or through outside vendors, problems can occur as the result of "cost saving measures". Commercial cleaning companies, although well-meaning, simply do not have the training, expertise or experience to safely treat outdoor sculpture. The MHS provides the overall knowledge and skills necessary to properly conserve and preserve these important historical and artistic objects for many generations to come. This collaboration is beneficial to the State, the outside vendors who are involved with the projects, MHS conservators, and the specialty of sculpture conservation. In the end, it is the people of Minnesota who benefit the most from having safe, stable monuments to see and enjoy.

Acknowledgements

The author would like to thank Ms. Sherelyn Ogden, Head of Conservation, MHS, for reviewing and editing this article. Thanks go to Tom Braun, Associate Objects Conservator, MHS, for presenting the original paper on this subject for me at the 30th AIC Annual Meeting OSG session in Miami, June 10, 2002. Thanks go to Mr. Ted Bores, Conservation Technician, Daniels Objects Conservation Laboratory, for all his work on the photographic reproductions for this article. Finally, great appreciation goes to Ms. Carolyn Kompelien, for without her tireless efforts and dedication there would not be a State Capitol Mall Sculpture Conservation Program, *de facto* or otherwise.

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Appendix 1

STATE CAPITOL MALL SCULPTURE CONSERVATION AND MAINTENANCE PROGRAM: LIST OF SCULPTURES AND CURRENT CONDITIONS

LIST PREPARED AND MAINTAINED BY: Paul S. Storch, Senior Objects Conservator UPDATED: May 26, 2000; July 9, 2001; September 2002

The following is a chart form for tracking the continuing conservation and maintenance of the extant, new installations, and proposed sculpture gardens and memorials on the Mall. It summarizes what has been or not been done to most of the sculptures. This is a working document and can be corrected and updated at any time. Please submit all comments and corrections directly to the author.

	······			
<u>Monument</u> C	urrent status	Cons. Date Cu	irrent action Prop	osed action
Columbus	Conserved; dusty;	1992, 1994	May 25, 2000:	Continue maint.;
C. Brioschi, 1932	spot corrosion on		"annual maint."	wax and Incralac
	lower areas of		By Contractor:	need stripping in
	robe, rope, and		wiped surfaces	certain areas-
	feet.		with toluene,	repatinate and
			resprayed with	recoat with
			Incralac.	Incralac only.
Leif Erikson	Conserved; dusty;	1996	annual maint. In	Continue maint.;
1949	coating spalls on		2001 by	granite base needs
	horizontal self-		Contractor	remortaring; repair
	base surface			concrete at base.
	where snow			Proposed treatment
	accumulates.			for FY03-04
"Spiral for Justice"	Improperly	1996	no maintenance;	refinish surface
Roy Wilkins	treated/cleaned by		annual condition	completely;
Memorial, 1997	artist; not		assessment and	conserve and coat;
	conserved;		'monitoring'; Cl-	establish annual
	streaky, uneven		test done in	cleaning and
	appearance; Cl-		Spring 1999: +	maintenance
	corrosion on tiles		results;	program.
			deterioration of	Contractor will
			surfaces is	submit a proposal
			worsening,	and budget
			structural	estimate to CAPPB
			damage to three	
			door on exterior	
			of the wall	

Monument	Current status	Cons. Date	Current action	Proposed action
				1

[1	1 1000		1
Charles Lindbergh	unstable in certain	surveyed 1989;	Cleaned and spot	annual cleaning
	areas: streaks	conserved 1999	repatinated	and maintenance
	from bird		August; coated	procedures before
	droppings.		with carnauba	July each year.
			wax; grantite	
			pavers reset;	
			May 2000:	
			cleaned overall	
			and re-coated	
			with wax. June	
			2001: maintained	
	corroded overall,	surveyed 1989;	MP Water	annual cleaning
Olson Statue	patina obscured	Conserved 1999	cleaned,	and maintenance
1953			repatinated and	before July each
			Incralac coated	vear
			in August 1999;	-
			pavers reset;	
			May 2000:	
			cleaned	
			retouched	
			Incralac. July	
			2001: maintained	

Monument	Current status	Cons. Date	Current action	Proposed action	
Johnson	corroded overall;	surveyed 1989;	MP Water	annual cleaning	l
Assemblage (5)	patina obscured;	Conserved 1999	cleaned,	and maintenance	I
1914	scythe blade		repatinated and		
	missing		Incralac coated		
			in July-Aug.;		
			granite cleaned,		
			stair support		
			repaired;		
			recaulked joints;		
			blade recast and		
			reattached. May		
			2000: 1st annual		
			maintenance:		
			cleaned overall,		
			re-patinated		
			corroded areas;		
			recoated with		
			gloss Incralac to		
			correct surface		
			texture. July		
			2001: maintained		

Vietnam	Examined in	None; regular	Plant Management	Establish general
Memorial plaza	1999; slight water	assessments	will cease to pile	cleaning and
1992	staining on NW		snow directly	maintenance
	corner of		against limestone	program: repair
	limestone; several		wall.	of lower margin
	spalls of		July 2001: black	of the limestone;
	limestone around		staining on roof of	recaulking when
	base of walls and		"house": requires	needed.
	"house".		cleaning	
USS Ward Gun	Painted	Surveyed in 1989;	None	Complete
		Condition		condition
		assessment for		assessment;
		FY03-04 work		Remove paint and
		done on 9/9/02 by		completely
		PSS		conserve; coat
				properly; clean
				and maintain on
				an annual basis.

Monument	Current status	Cons. Date	Current action	Proposed action
Women's Sufferage memorial 2000-2001	under construction	n/a	July 2001: Artist installing steel(?) lattice work 'wall'. MHS requires material information and maintenance recommendations from artist and fabricators.	establish annual cleaning and maintenance program
Wall war memorial plaques; in front of Veterans' Service Bldg.	Various conditions, several are new; all appear to be uncoated	examined in 1999	None	Establish regular cleaning, conservation, and maintenance program
Liberty Bell replica	Dusty, minor corrosion	Surveyed in 1989	None	Establish regular cleaning and maintenance program.
"Earthbound": marble sculpture in front of Veterans' Service Bldg.	Dusty; sugary surface in 1989	Surveyed in 1989	None	Establish regular cleaning and maintenance program.
Korean War Mem. 1998	Newly installed (8/1998); patinated; coating applied (?)	N/a	None	need documentation on artist's intent,materials and maintenance protocol; establish annual maintenance: cleaning, and maintaining coating integrity. Proposed treatment and coating in FY03-04

Monument	Current status	Cons. Date	Current action	Proposed action
Peace Officers Memorial Fountain and Plaza 1995	Light no longer functions- inherent vice in design; corroding iron bolts in top of fountain basin causes staining on granite; rusting on galvanized duct	May 1999: cleaned all sides of granite fountain block with 10% oxalic acid (aqueous)	Plant managment is working on getting iron staining sources removed from the fountain; May 2000: recleaned with 10% oxalic acid solution; all sources of corrosion not yet removed from the fountain mechanism. July 2001: corrosion source still has not been removed; granite is stained overall and requires cleaning.	Re-clean the granite block surfaces after the rust sources are removed. Implement annual maintenance procedures. Annual cleaning appears to be done by Plant Management
Promise of Youth Fountain bronze sculpture 1958	Sculpture was bolted in closed leaf position due to maintenance problems and inherent vice in design. Corroded iron alloy components; patina on bronze obscured by corrosion.	Conservation in progress 1999- early 2000; maintained in 2001	Sculpture removed from base for conservation; surface treatment; structural treatment; possible support for leaves being considered; reinstallation on redesigned base in redesigned fountain pool in Spring 2000. June 2001: maintenance.	Annual cleaning and maintenance; regular fountain pool maintenance.

agreeded averally	and the second sec		
patina obscured	surveyed 1989; Conserved 1999	MP Water cleaned, repatinated and Incralac coated in July-Aug., granite cleaned; stair support repaired; recaulked joints. May 2000: cleaned overall; corrected corrosion spots and incorrect surface texture with gloss Incralac. July 2001: maintained	annual cleaning and maintenance
conserved; becomes dusty and dirty over the winter; rust forms on screen around base support; minor pitting on chariot wheels, base, and undersides of the horses.	1995	Annual maintenance and documentation. July 9, 2001: testing of re- gilding and mock-ups commenced by the Contractor in SeptOct. 2001; overall cleaning will be done on accessible areas.	Continue maint.; eventual regilding of selected areas; front areas need cleaning; continue to monitor gilt panel tests. Spot regildjng to continue in FY 03- 04
corroded overall; patina obscured	surveyed 1989; resurveyed 1999	None	full conservation: prob. Re- galvanization, repainting; annual cleaning and maintenance
	conserved; becomes dusty and dirty over the winter; rust forms on screen around base support; minor pitting on chariot wheels, base, and undersides of the horses. corroded overall; patina obscured	controlled overall, patina obscuredsurveyed 1989, Conserved 1999conserved; becomes dusty and dirty over the winter; rust forms on screen around base support; minor pitting on chariot wheels, base, and undersides of the horses.1995corroded overall; patina obscuredsurveyed 1989; resurveyed 1999	corrocted overall, patina obscuredsurveyed 1939, Conserved 1999Mr watch cleaned, repatinated and Incralac coated in July-Aug., granite cleaned; stair support repaired; recaulked joints. May 2000: cleaned overall; corrected corrosion spots and incorrect surface texture with gloss Incralac. July 2001: maintainedconserved; becomes dusty and dirty over the winter; rust forms on screen around base support; minor pitting on chariot wheels, base, and undersides of the horses.1995Annual maintenance and documentation. July 9, 2001: testing of re- gilding and mock-ups commenced by the Contractor in SeptOct. 2001; overall cleaning will be done on accessible areas.corroded overall; surveyed 1989; patina obscuredsurveyed 1989; resurveyed 1989; resurveyed 1999None

Appendix 2. Disaster Response Policy and Procedures for SC Mall Sculptures. Developed in 1994 and distributed to MN State Capitol Security and Plant Management.

1. Response:

The discoverer of the vandalism should contact Capitol Security, who will then contact the State Capitol Site Manager (MHS). If The Site Manager is not available, contact the Senior Objects Conservator and the Head of Conservation, if the Senior Objects Conservator is not available.

The area should be roped off as soon as possible. Determination should be made as to whether it is a crime scene, and if so, the St. Paul Police Department should be called.

The first response of the State Plant Management painters will be limited to wicking up any paint in order to prevent it from dripping onto other surfaces and from seeping into joints. No attempt should be made to remove the paint.

If an outside cleaning contractor is called in before the MHS conservation staff can arrive for a complete assessment of the situation, they must wait. The MHS conservator who responds to the call will determine the extent of the damage, the current condition of the object, and recommend the cleaning procedure to be followed. The conservator will supply any cleaning solutions that will be used. The conservator will determine if high pressure water cleaning is applicable to the problem. Commercial cleaners and degreasers such as C&H 744 Degreaser will not be used.

2. Cleaning Methods:

The specific cleaning procedure will vary depending on the nature of the paint binder, and the nature and condition of the object surface.

Water should be made available by State Plant Management staff responding to the call in order to clean water soluble latex-based paints.

Oil-based paints will be cleaned with solvents or other cleaners to be determined by MHS conservation staff.

Containers for waste rags and other expendable cleaning materials should be provided by the State Plant Management division staff and be removed immediately from the site after the cleaning is finished.

After the cleaning is completed, the MHS conservation staff will determine what applicable follow-up procedures will need to be done.

The damage and subsequent clean-up and treatments will be documented in writing and by photographs and will become part of the MHS conservation documentation for the affected sculpture or monument. Any other applicable documentation generated by other state agencies or outside contractors may also become part of those records.

3. MHS Staff to Call:

State Capitol Historic Site Manager Senior Objects Conservator Head of Conservation



- **★ 1**. Quadriga 1906
 - 2. Knute Nelson 1928
 - 3. John Johnson 1912
- 🗙 4. Leif Erikson 1949
 - 5. Floyd B. Olson 1958
 - 6. Charles Lindbergh 1985
- **★ 7.** Roy Wilkins Memorial 1995
 - 8. Monument to the Living 1982
 - 9. Minnesota Vietnam Memorial – 1992
- X 10. War Memorial Plaques Court of Honor

- 11. Veterans Services Building Memorials
- 12. The Peace Officers Memorial – 1995
- ★ 13. Korean War Veterans Memorial – 1998
 - 14. The Women's Suffrage Memorial Garden – 1999
- X 15. Christopher Columbus 1931
 16. Judicial Plaza 1995

Figure 1. Plan of MN State Capitol Mall and list of monuments, from the official visitor guide. Monuments marked with an 'X' are mentioned in this article.







Figure 2. South view of MN State Capitol Mall. Monuments to Governors Nelson and Johnson are in the left foreground.

Figure 3. Cast bronze Korean War monument figure.



Figure 4. Detail of the cast bronze *Promise* of Youth fountain, after conservation and reinstallation in 2001.



Figure 5. View of the Roy Wilkens memorial plaza, *Spiral for Justice*, in 2002, showing dark weathering surfaces.


Figure 6. Christopher Columbus monument.



Figure 7. The author taking photomicrographs of the medium water pressure cleaning test results on the self base of *Christopher Columbus*, in 1992.



Figure 8. FOC, Inc., re-patinating *Christopher Columbus* in 1992.



Figure 9. Self-base of Christopher Columbus masked off for the cleaning tests, 1992.





Figure 10. Chest area of *Christopher Columbus* showing metal surface after solvent stripping the layers of Incralac and wax for spot treatment to repair paint damage caused by vandalism, 1994.



Figure 11. The author performing annual maintenance on *Christopher Columbus*, 1995.



Figure 12. CTA staff cleaning *Leif Erickson*, 1996.



Figure 13. CTA staff applying Incralac lacquer to the self base of *Leif Erickson*, 1996.



Figure 14. CTA staff taking coating thickness measurements on the head of *Leif Erickson* after treatment, 1996.



Figure 15. Delfesko Positest 6000 coating thickness instrument with remote probe (on right) and HP infrared printer (on left).



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1 LE1998
Batch
Capture date: 10/1/98 4:06:15 PM
Gage model: 6000FNSE S/N: 20246
  Username: PStorch
  Operator: PStorch
       Part: Leif Erikson: PRDrapery
 Coating: Incralac
Substrate: NonFE
   Process: Spraying
           N:
                   10
                    5.96 mils
       Mean:
   Std Dev:
                    1.8898 mils
        Max:
                    8.4 mils
        Min:
                    3 mils
        USL:
                 ___
         LSL:
                  ___
Annotation:
PR Drapery by Bicep. The readings were taken by P. Storch and Chris, CTA, 9/16/98 as part of the 2nd year's CTA maintenance contract. The coating thickness varied
from 1.5 to 2.0 mils.
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Figure 16. Graph of Positest instrument thickness data, Leif Erickson sculpture.



Figure 17. Rooftop view of the Quadriga (*Progress of the State*) on the Minnesota State Capitol building.



Figure 18. Detail of spot corrosion on the gilded surface of the Quadriga, underside of a horse, 1999.



Figure 19. Gilding test panel set up on the State Capitol roof to track weathering changes, 2001.



Figure 20. The author performing annual maintenance on the Quadriga, washing and waxing gilded surfaces, 1998.





Figure 21. (upper left) Detail of the corroded surface on the rear of the chariot, 2001.

Figure 22. (upper right) Detail after mechanical removal of the spot corrosion down to the metal surface as part of the regilding tests, rear of the chariot, 2001.

Figure 23. (lower left) Rear panel of the chariot after priming and regilding during regilding tests, 2001.

AESTHETICS, CONSERVATION AND MAINTENANCE OF OUTDOOR BRONZES

W. T. Chase

1. Introduction

Today I'm going to talk a little about aesthetics, conservation, and maintenance of outdoor bronzes. I'd like to thank many people for contributing to this talk, especially The Fairmount Park Art Association, Penny Bach and Laura Griffith, Steve Tatti and Kurt Solmssen, and Nick Veloz. Much of this paper has been drawn from the draft report, Assessment Study Report - Fairmount Park Art Association's Outdoor Sculpture Conservation and Maintenance Program: Draft 2, W. T. Chase, Chase Art Services, February 23,2001, and from my short article in *Save Outdoor Sculpture Update, Fall, 2001, Volume 12, No. 2, p. 7,* "A Program that Works – Fairmount Park Art Association's Maintenance Program." All photographs are by the authors except as noted.

When I started on an assessment of the Fairmount Park Art Association's outdoor sculpture maintenance program two years ago, I had a nice discussion with Rene De La Rie of the National Gallery. Rene said that I should pay particular attention to aesthetics in looking at the treatment problems. We agreed that being more rigorous in terms of the aesthetics of ourdoor bronzes would be very useful. As it turns out, I feel more like we're hanging on by our teeth in terms of aesthetics, and reasonable-looking bronze statues is a good side benefit of good treatments.

2. The Maintenance Program

The Fairmount Park art association's sculpture maintenance program began treatments of outdoor sculptures in 1983. Setting up a program was in the works for a couple of years before this. The idea was to treat and maintain a group of sculptures in Philadelphia as an example of what could be done with a regular maintenance program. Steve Tatti has been the conservator throughout, and he has an assistant, Kurt Solmssen, who performs the actual maintenance once a year.



Figure 1. Kurt Solmssen working on *Welcoming Freedom* (2002).

Initial treatment was to clean the sculptures with low-pressure water and nonionic detergent, rinse and dry them. The sculptures were then heated with a torch and wax (a mixture of microcrystalline waxes – see box) was applied. This was repeated two or three times until the sculptures were saturated. The wax was allowed to cool and then was buffed for appearance.

Steve Tatti's Wax Mixture

- 85% Bareco Victory Brown microcrystalline wax
- 10% Bareco 2000 polyethylene wax
- 5% Cosmoloid 80H wax

Fig. 1 shows Kurt Solmssen heating the sculpture *Welcoming Freedom* at the Samuel Memorial before reapplying wax (photograph taken in 2000). During the annual maintenance program, each sculpture was inspected and then washed. Sculptures near roads or in areas that seemed dirty were also cleaned with mineral spirits. After they were dry the sculptures were heated with a torch, more wax put on where needed, and then buffed.

3. A Test of the Efficacy of the Treatment

We mentioned saturation above. Fig. 2 below shows the sculpture *Stone Age in America* before treatment in 1982 and after treatment in 1983. You can see that the wax has saturated the powdery green and darkened the whole statue, making it easier to read the sculptural form. (Photographs by Franco Khoury.)



Figure 2. Left, Before treatment (1982); right, after treatment (1983).

As part of the assessment of the maintenance program, we decided to test clean an area to see how reversible the process was and whether subsequent corrosion had taken place under the wax. Kurt test-cleaned an area on the head and shoulder of the child. The photographs reproduced in Fig. 3 show the sculpture before treatment in 1983 (on the left) and after 17 years of maintenance (on the right). The black islands and green background appear to be unchanged.



Figure 3a, b. Detail of the child's face: left, before treatment; right, after removal of wax in 2000. No change in the size and position of black spots can be seen. Photograph on left by Franco Khoury, 1982.

Figs. 4a and 4b, details of the two photographs, show that the islands are unchanged. Even the fine pores within the islands look the same. We couldn't detect any difference. As far as this test goes, the maintenance program seems to be performing perfectly.



Figure 4a, b. Enlarged area, detail of the child's cheek. Left, before treatment in 1982; right, after removal of wax in 2000. Photograph on left by Franco Khoury, 1982.

3.1 Pinholes

Some problems were, however, noticed. There are failure spots in the wax coat which lead to pinholes with corrosion. These disappear in the annual waxing, but are indicative of something happening below the surface. A good example can be seen on the Frederic Remington *Cowboy* seen in Fig. 5. "Pinholes" in the existing wax coat, with bright green corrosion coming up through the pinhole, can be seen in Fig. 6a. My index finger is in here to indicate scale. After heating and rewaxing, the pinholes disappear (see Fig. 6b).



Figure 5. *The Cowboy*, by Frederick Remington. The area shown in Figs. 6a and 6b is in the drapery near the saddle.



Figures 6a, 6b. *The Cowboy*, by Frederick Remington. Fig. 6a (top) shows the pinholes filled with corrosion. Index finger indicates the scale. Fig. 6b (bottom) shows the same spot after the old wax has been cleaned and heated. The spots have disappeared.

3.2 Crizzling of the Wax

In some cases the wax crizzles or develops a fine crackle pattern. This can be associated with water leaks from the inside of the sculpture, but it also appears to happen in areas devoid of water leaks. It's a phenomenon the needs further study. The crizzled wax comes off in washing, and any that does not come off is reformed when the sculpture is heated. In Fig. 7a, wax crizzling along with graffiti can be seen on the lower part of the *Welcoming Freedom* statue. Fig. 7b shows wax crizzling in more detail, with a centimeter scale. The wax can be seen not to be adhering to the bronze; little white flakes are forming. With reheating and the addition of more wax, they will disappear.

4. What Happens if Maintenance is Stopped?

Of course, if you stop the maintenance program, these problems are not going to be ameliorated in the annual maintenance and they will continue.

If maintenance is stopped, the wax begins to break down. Initial breakdown seems to be in the form of pinholes like those we saw in Fig. 6a, above. These pinholes allow corrosion to proceed at isolated spots. Since the rest of the surface is protected, corrosion at the individual spots can be quite aggressive. Fig. 8a shows some of the corroded spots from pinhole breakdown of the wax on the *Galusha Pennepacker* statue along Franklin Parkway in Philadelphia. After removal on the wax with walnut-shell blasting (Fig. 8b), the spots are still visible. They disappear with a subsequent application of wax (Fig. 8c).

In a later stage, the wax can be seen to come off as a brittle film, leaving larger and larger areas of the sculpture unprotected. This sort of failure is seen in Fig. 9a-c, showing various areas of the *Washington Monument* in Philadelphia.

5. Improved Methods

A number of people have been looking for improved methods for protecting outdoor bronzes. Nick Veloz's wax method gives a coating of wax that lasts 3 - 5 years. Nick starts with walnut shell blasting, which removes any powdery corrosion and evens out the surface appearance of the sculpture. Then wax is applied, first by hand and second with a sprayer. The individual wax coats are heated and, finally, buffed. As you

Nick Veloz's Wax Mixture

- 71% Bareco Victory White (or brown, for brown wax)
- 13% Polywax 2000
- 13% Petronauba (synthetic carnauba)
- 03% Polywax 500

will see, this wax seems to fail more generally than in pinholes, another feature that is better for the sculptures. Nick also points out that the wax seems to last longer in subsequent applications. The first application after walnut shell blasting won't last as well as the application applied three years later as part of a maintenance program.



Figures 7a and 7b. Wax crizzling and graffiti on the *Welcoming Freedom* statue. Fig. 7a shows the crizzling and graffiti on the lower back on the statue. Fig. 7b shows crizzling at a much higher magnification (cm bar for scale). The crizzled wax looks crystalline.



Figure 8a, b, c. Wax failure and subsequent treatment on the statue of *Galusha Pennepacker*, Benjamin Franklin Parkway, Philadelphia.

Fig. 8a. Corroded spots from pinpoint failure of the wax coating.

Fig. 8b. The statue has been blasted with walnut shells to remove the wax and even out the patina, but the smaller light spots are still visible.

Fig. 8c. The same area after application of a wax coat.



Figure 9a, b, c. Various areas on the *Washington Monument*, Eakins Oval, Benjamin Franklin Parkway, Philadelphia, showing longterm failure of the wax coating.

Fig. 9a. The reclining figure of America where the wax is failing to protect the sculpture.

Fig. 9b. Detail of an area on the leg; old channels from precipitation can be seen running vertically. Some of these are bright green, showing that corrosion is again taking place.

Fig. 9c. The mane of one of the buffalos. Wax loss and subsequent corrosion is quite severe in this area.

Figure 10a shows another statue in Fairmount Park, *The Medicine Man*, after five years outside with Nick's wax in place. Here you can see wax failure in the lower portion of the headdress and a few other spots. The wax has lasted amazingly well. Fig. 10b shows what the statue looks like after rewaxing. It has a nice, even, deep green patina.



Figure 10a. *The Medicine Man*, Fairmount Park, Philadelphia. After five years of exposure.



Figure 10b. The same sculpture after rewaxing.

Fig. 11 is a closer view of the proper right leg of the statue, showing how the wax deterioration is rather even. A comparison of the deteriorated wax coat (Fig. 11a) and the rewaxed appearance (Fig. 11b) shows that the deterioration disappears on rewaxing.



Figure 11a, b. Details of Figure 10. The generalized failure of the wax coating can be seen in Fig. 11a on the left. The deterioration disappears after rewaxing.

6. Discussion

In terms of conservation, or simply preserving what's there, the Tatti treatment may be better because no blasting or strenuous cleaning techniques are used. On the other hand, this treatment requires annual maintenance. The wax seems to begin to break down after about a year, at least in spots. If it is left for two years, the corrosion begins to be serious. However, as long as the maintenance cycle is kept up, this is a good way to conserve outdoor bronzes.

The treatment by Nick Veloz lasts longer, but starts with walnut-shell blasting of the loose green material. After walnut-shell blasting, the sculptures are more even in appearance. The wax mixture that Nick uses also seems to be more transparent, yielding a more colorful patina, often a very nice green.

Part of the longer life of the wax in Nick Veloz's treatment may be due to the nature of a different wax mixture. Nick is now putting Tinuvin in the wax in an attempt to get it to last even longer. Part of the longevity, however, is probably due to the better preparation of the substrate and the removal of powdery corrosion products. Walnut shell blasting is producing a small permanent change to the surface of the sculpture, but it is also making it receive the wax better so that the subsequent wax coat will last longer. There are no indications that original surface is being removed from the sculptures -- tests on disposable old bronze show that any cuprite layer on the surface is preserved by walnut shell blasting. Non-adherent corrosion is, however, being removed.

So here we have two treatments, one less intrusive but also maintenance-intensive, and the other slightly more intrusive but with a better maintenance record. In deciding which of these to apply, I believe we need to consider aesthetics, conservation considerations, and maintenance. Budgetary considerations also loom large. Perhaps we really need to consider outdoor sculptures not as fine art but as artistic structures which should be preserved the best way possible. The last thing I'll mention in this talk is the obvious need for future research to improve treatments and to help us define better ways for long-term outdoor sculpture preservation.

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THREE CASE STUDIES OF OUTDOOR SCULPTURE WITH PROBLEMATIC INTENT ISSUES

Michael Belman

1. Introduction

In the three case studies discussed in this paper, problematic intent issues will refer to confusing aspects of an outdoor work's design, intended use and intended role that result in recurrent or accumulated damage. This term will also relate to the overall susceptibility of an object to abuse or harm, such as having weak construction or a vulnerable location.

The first example, *The New York State Fallen Firefighters Memorial* by Robert Eccleston, is a monument that is shared by numerous groups, each often commemorating different time periods. The integral base under the statue invites the public to continually place memorial items in direct contact with the bronze surface. The second case, *Trio* by George Sugarman, involves a sculpture that was specifically designed, painted and sited by the artist to invite physical interaction. In return it receives a constant battering from vandalism, skateboarding and BMX riding that surpasses what could have been anticipated. The third instance, *Formula Compound #1* by Dennis Oppenheim, was an imposing, multi-part installation that was acquired by a small state college for a one-time fireworks performance. No future role after the performance was ever determined, and the sculpture was essentially forgotten and allowed to degrade in a field for two decades.

Case Study 1. The New York State Fallen Firefighters Memorial

The New York State Fallen Firefighters Memorial is an 11 foot tall, bronze sculpture of two firefighters rescuing their injured comrade. It was cast at the Tallix foundry in Beacon, New York, and unveiled in October of 1998 at the Empire State Plaza in Albany, New York (Fig. 1). Behind the sculpture is a gray granite wall that has been sandblasted with the names of the men and women of the New York State Fire Service who have died in the line of duty (New York State Fallen Firefighters Memorial Committee, Inc 2001). Individual firehouses, fraternity organizations and auxiliary groups share the memorial. It serves as a backdrop for special ceremonies and becomes the symbol for those that died and an object of comfort.



Figure 1. *The New York State Fallen Firefighters Memorial*. Robert Eccleston, 1998, bronze. (11' 4" x 6' 5" x 7' 3") Empire State Plaza Art Collection.

In the process of maintaining the memorial, objects conservators from the Williamstown Art Conservation Center observed that the public often places flowers both against the wall of names and on the wide, flat base surrounding the sculpture. It is unclear if it was ever intended for flowers to be put on the base, or if they should only be placed against the wall.

During a week of hot summer days in July of 2001, the sculpture was given what would be considered a fairly standard cleaning and hot wax treatment. Existing patches of flaky green corrosion product were removed using a 2% solution of Orvus in tap water, and a 0.5 solution of diamonium citrate on stiff brushes and cotton cloths. The treatment produced a shiny, saturated black surface with no visible traces of corrosion.

The public really seems to like the memorial. It is the only representational work in an immense plaza that contains numerous abstract expressionist sculptures. People would constantly come up and inquire about the sculpture during the treatment. The abstract art in the plaza is often vandalized. The Firefighters Memorial is left alone. After the World Trade Center collapse, the

objects lab in Williamstown received a phone call from the offices of the Empire State Plaza Art Collection. In the outpouring of grief after the disaster, flowers, wreathes, figurines, clothing, candles, letters and bells were being heaped on the base of the firefighter sculpture causing new bright green corrosion (Figs. 2 and 3). The conservators inquired as to whose responsibility it was to remove the items, assuming that they were probably important to some specific groups, and they would want it done respectfully. It turned out that there was no set plan for collection.



Figure 2. *The New York State Fallen Firefighters Memorial*. The base of the sculpture shows heaped memorial items following September 11th. Photo taken September 15th, 2001

A few weeks later, the New York State offices informed Williamstown staff that a rededication ceremony was scheduled at the memorial on October 9 during Fire Prevention week. The ceremony was to be attended by George Pataki and Rudolph Giuliani to honor the firefighters who had died in 2000. The objects conservators were asked to make the sculpture presentable for the ceremony.

The 911 memorial items were set aside and the corrosion was removed again (using the same technique as before), though this time there was some visible damage to the patina. The conservators felt it important to not interfere with the outpouring of emotion, and after the treatment, everything was carefully replaced.



Figure 3. *The New York State Fallen Firefighters Memorial*. Bright green corrosion from the post-September 11th memorial items. October 5th, 2001 cleaning for the Rededication Ceremony.

A Williamstown representative attended the ceremony only a few days later, and observed that someone had cleared off the 911 memorial objects and a new group of more formal, funeral type flowers were accumulating (see Fig. 4). It was reasoned that those who were lost in the World Trade Center in 2001 should not eclipse the memory of the firefighters who died in 2000. There were many speeches given by chaplains, rabbis, the governor and other politicians. Fig. 5 shows the dramatic highpoint, when wreathes were laid on base of the sculpture accompanied by a bagpipe. Objects conservators visited the plaza during the week after the ceremony and noticed that the 911 memorial objects were back on the sculpture again.



Figure 4. *The New York State Fallen Firefighters Memorial*. Robert Eccleston. Overall view with flowers commemorating the firefighters that died during the year 2000. Photo taken October 6th, 2001.



Figure 5. *The New York State Fallen Firefighters Memorial*. The dramatic highpoint of the Rededication Ceremony, when wreaths were laid on the base of the sculpture, accompanied by a bagpiper. Governor George Pataki can be seen in the background. Photo taken October 9th, 2001.

It is unfortunate that the design of the base can invite recurrent damage. At the same time, however, it seems completely appropriate that the accumulated wear comes from those who are in the process of remembering. While the wall contains the names of the fallen, the sculpture provides a more tangible visual focal point. In the act of placing flowers on the base, mourners intuitively get a different sense of their loved ones heroic sacrifice. The accumulating wear can be viewed as evidence of this interaction.

Williamstown Art Conservation Center recommended that New York State develop a set procedure for sharing the monument, one that would involve sensitively collecting the memorial items in order to minimize the prolonged contact that causes such damage. A protective mat could be laid out on the base during ceremonies or other periods of remembrance. Another solution, although one that would significantly change the current use pattern, is to set a small sign into the base respectfully asking to please put flowers against the wall.

Case Study 2. Trio

The next case study, *Trio*, by George Sugarman, is one of the artist's earliest outdoor pieces. The 10 foot tall by 32 foot long by 13 foot wide, aluminum work was installed at the Empire State Plaza in 1976 (Fig. 6). Sugarman himself suggested the sighting of *Trio* in its location along a busy pedestrian walkway. The catalogue of the Empire State Plaza Art Collection describes Sugarman's sculpture as "inviting public participation", and states that, "Sugarman believes that a one-to-one physical experience is the basis for....the intellectual aspects of art" (Easton et al. 1987, 190).



Figure 6. *Trio.* George Sugarman, 1968-71, painted aluminum. (10' x 32' x 13') Empire State Plaza Art Collection.

When the sculpture arrived from the fabricator, structural cracks had developed in the relatively small contact points where the arching shapes come together. As early as 1979, a condition report from the Albany Institute for History and Art pointed out that since its installation, the weight of people climbing on the un-reinforced sculpture had worsened the original damage. Fabricated from a weak aluminum alloy, the report recommended that structural repairs be made by rewelding the cracked areas and that the work should be bolted down in an area that is not as heavily traveled by pedestrians. The report also stated that some attempt should be made to educate the public that *Trio* is a sculpture and not a Jungle Jim, and that periodic cleaning should be undertaken to remove hand prints, grease and accumulated grime (Albany Institute for History and Art 1979).

Fifteen years and numerous maintenance campaigns later, on March 25th, 1993, between 4 and 5:30 am, *Trio* was rolled 25 feet into an empty reflecting pool nearby on the plaza. There was speculation that Grateful Dead fans may have damaged the sculpture, as the band was playing at the nearby Knickerbocker Arena, now called the Pepsi Arena, earlier that night. A spokesperson for the New York State Offices was quoted as saying "There were 60,000 Grateful Dead fans in the area, and we can't rule out that possibility" (Quinn 1993, 11).



Figure 7. Trio, split in half following the catastrophic March 25th 1993 act of vandalism.

The Williamstown Art Conservation Center condition report after the incident described the sculpture as having broken in half with extensive paint loss overall Fig. 7). The report mentions

that the work had never been bolted down because of the complexity of the plaza substructure. Conservation treatment ensued. The two halves were welded together and the entire sculpture was anchored into the plaza with four threaded stainless steel bolts. Dents and paint losses were filled and spot primed, and the object was completely repainted with three coats of a polyurethane enamel that was recommended by the artist (Williamstown Art Conservation Center 1993).

Only seven years later, in the summer of 2000, Trio needed another major restoration campaign to repair cracks and paint loss not only from climbing, but also from skateboarding and BMX riding. Immediately following the final paint application in this treatment, the sculpture was overrun with black footprints from vandals (Fig. 8). This occurred very quickly, within ½ hour of application, despite stanchions and wet paint signs. Paint was reapplied locally to cover the footprints (Holbrow 2002).



Figure 8. *Trio*. Footprints of a vandal in freshly applied polyurethane paint, following the Summer 2000 treatment.

Now that *Trio* is bolted down, the structural damage accumulates slowly relative to the paint damage. Although Empire State Plaza sits in the shadow of the New York State Capitol Building, surprisingly, there is no regular security presence. As a result, the sculpture is subject to daily raids by vandals. There are sure to be new gouges and scratches to repair for the 2002 outdoor sculpture season.

It is difficult to solve this object's problems entirely. Re-sighting it to a less traveled area is not a great option, considering the artist personally chose its current location. It seems inappropriate to block it off with barriers that would limit public interaction and obstruct its view. It is difficult to determine if Sugarman intended the sculpture for just sitting and a little climbing, or if it was meant for more intense contact.



Figure 9. Trio. A typical example of the intended public interaction with the sculpture.

On any given day there will be children playing on *Trio* (Fig. 9). Tourists inspect it closely when they walk by. It serves as a bleacher for a nearby performance space on the Plaza and gives off a lot of stimulus with its playful form and color. Much of the wear that *Trio* accumulates is evidence of this interaction. However, skateboarding and BMX riding may be beyond what the artist envisioned. It may be possible to install an unobtrusive barrier such as staggered rows of low concrete bumps that will still allow physical contact with the sculpture and keep out skateboarders and BMX riders.

Case Study 3. Formula Compound #1

The last case study is *Formula Compound* #1 by Dennis Oppenheim. Acquired in 1983 by the Brainerd Gallery at SUNY Pottsdam College in northern New York State, the multi-part

installation provided the base from which a fireworks performance was set off. The tracks served to channel the fountains of sparks, redirecting them and bouncing them off banks of panels. Fig. 10 shows the appearance of the work just after its construction. Some of the parts, such as the towering pinwheels visible in the image, were propelled during the performance. It occupied a large field near the college and covered an area of approximately 70 feet by 70 feet; the tallest structure was approximately 25 feet high. It consisted of 20 different elements of low alloy steel, fabricated from welded perforated sheets, ribbed tracks, angle iron, pipe and cable painted grey, green, red and black (Williamstown Art Conservation Center 2001).



Figure 10. Formula Compound #1. Dennis Oppenheim, 1983, painted steel and aluminum. (70' x 70' x 25') Collection of the Roland Gibson Gallery, SUNY Potsdam College. Overall view of the sculpture just after its installation at Potsdam College in 1983.

The first *Formula Compound #1* fireworks performance was held in Battery Park in lower Manhattan in1982 with mixed success. During that showing, some of the rockets accidentally shot into the audience (Crary 1983). Oppenheim felt that the piece should only be fired once and that it was unnecessary to light it again. He found a home for the sculpture at Potsdam College, who, inspired by the previous performance, made grand plans to re-ignite it on their own as part of an annual fall fireworks celebration (Price 2002).



Figure 11. Formula Compound #1. The Fall 1983 fireworks performance at Potsdam College.

Six thousand people attended the display, which was for the most part successful. Apparently, Oppenheim's assistant, who attended the performance on the artist's behalf, said that the fireworks did not capture the true essence of the piece. Afterwards, the college was left with the lingering material from *Formula Compound #1* as well as installation bills, and they turned their attention away from the spent sculpture to other emergencies. The staff changed within the art department and in time the sculpture was largely forgotten, eclipsed by budget droughts that are common at small state colleges. Even at the time of the fireworks display there was a difference of opinion as to whether or not the piece was mean to be permanent. After the performance the artist was unreachable and the future role of *Formula Compound #1* and its intended life span were never clarified (Price 2002). Eighteen years went by, and the sculpture was brought back to the attention of the art department by Potsdam college groundskeepers, who claimed that it had become a safety hazard.

The Brainerd Gallery, now called the Roland Gibson Gallery, asked the Williamstown Art Conservation Center in August of 2001 to examine *Formula Compound #1* and draft a treatment proposal. The sculpture had fallen into a state of severe deterioration due to lack of maintenance. Numerous parts had tipped over, broken apart and were scattered about the field, lost and half buried in the grass (see Fig. 12). The mesh screens had badly rusted, as were many of the welded

joints of the ribbed tracks and ramps. Particularly unnerving was the large dangling cylinder, which was suspended on a single rusted cable from the supporting tower (see Fig. 13).



Figure 12. Formula Compound #1. Detail of steel elements that have collapsed after 18 years without maintenance.



Figure 13. Formula Compound #1. Detail of elements of the sculpture as they appeared in March 2002.

Whole sections of the reflector panels had been relocated and other elements visible in the original image, such as the towering pinwheels, now appeared to be missing entirely. Due to corrosion and weathering, much of the original paint was badly flaking or lost from the metal surfaces (see Fig. 14). Because no blueprints or other ground plans were available, the full extent of the damage was unclear. The size and weight of the steel elements, in particular the towers and dangling parts, made the sculpture a danger and a liability. The presence of empty beer bottles confirmed that the site had become a night time hangout spot for the Potsdam college students.



Figure 14. Formula Compound #1. The banks of panels showing corrosion, paint loss and missing pieces. March 2002

The college administration, the physical plant and many town residents voted to have the installation taken down. Oppenheim was finally reached and he assured Potsdam College that it was meant to be a permanent work, even though he had no idea of its condition or the vast monetary costs required for conservation treatment. Williamstown Art Conservation Center recommended that the Roland Gibson Gallery thoroughly document the current form and arrangement of the elements and then put them in storage until outside funding could be obtained to restore it on a new site (Fig. 15). The sculpture was dismantled in March 2002. The Gallery contacted several sculpture parks, but none of them wanted to take the installation. The work is unfortunately destined for the scrap yard (Price 2002).



Figure 15. *Formula Compound* #1. Overall view as it appeared in March 2002 before demolition.

It is interesting to imagine, even with a fully restored version, what future role the installation could serve in a field such as this. With its imposing look and sharp edges, is this piece an appropriate rallying point for students on a college campus, like an amphitheater? From afar, the sculpture does resemble some kind of obstacle course or playground. When viewed up close, it is evident that the construction is only adequate enough to allow the piece to remain standing. Judging from this medium weight manufacture, it is likely that the artist only ever intended *Formula Compound* #1 to be viewed from a distance, and walked around in a well-behaved manner. Considering that the sculpture's original role was part of a one-time performance, it is possible that documentary film footage of the fireworks would have been the most appropriate preservation.

Conclusion

The ideal situation for preventing the problems in these case studies would be to identify the potentially problematic aspects of the work before it is installed, during the artist's design and fabrication process. The sculpture's intended role, life span, specific design and material choices can be thoroughly weighed against the long-term effects of the ideal and non-ideal viewer and the outdoor environment.

The far more common situation is finding oneself with the inherited problem. In the case of *Formula Compound* #1, Dennis Oppenheim had accepted the terms of Potsdam College's

collections management policy. They were within their rights to dismantle the sculpture because in their eyes, it had become an expensive safety hazard and was no longer relevant or useful for exhibition or educational reference (Price 2002).

In the cases of the *Firefighter's Memorial* and *Trio*, coordinated usage procedures, maintenance plans and unobtrusive barriers certainly may assist in reducing their recurrent damage. It is also helpful when an artist is more accepting of changes or involved conservation treatments. But most importantly with outdoor sculpture intended for a specific use, it may be necessary for conservators to adjust their thinking to accept the heavier wear and maintenance as positive.

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AN OPPORTUNITY TAKEN: THE PROJECT DESIGN FOR A TECHNICAL STUDY OF 26 BRONZES IN THE EXHIBITION *ADRIAEN DE VRIES: IMPERIAL SCULPTOR* AT THE J. PAUL GETTY MUSEUM

Jane Bassett

1. Introduction

Through scientific analysis, consideration of historic background, and most importantly through careful and thoughtful observation, the conservator can add considerably to the body of knowledge on a specific work, artist, or school. Our role as observer and interpreter can make an important contribution, one that has recently gained broad acceptance in the field of European bronze connoisseurship. This paper summarizes the design of such a project undertaken at The J. Paul Getty Museum in Los Angeles.

In December of 1999, a landmark exhibition of bronzes by the Dutch artist Adriaen de Vries opened in Los Angeles following earlier venues in Amsterdam and Stockholm [1]. The exhibition included 39 bronzes by de Vries, accompanied by a small number of drawings and comparative sculptures (Fig. 1). Although relatively unknown to all but a handful of specialist scholars until recently, Adriaen de Vries was highly sought-after in his day, working for some of the most powerful patrons in Northern Europe. Born in the Hague in 1556, by the age of 25, de Vries was employed in the Florentine workshop of Giovanni Bologna (better known as Giambologna). He then worked as Chief Assistant with Pompeo Leoni on a commission of larger than life-size bronze figures for the Escorial. De Vries then travelled to Turin, Rome, and Augsburg, finally settling in the artistically dynamic court of Emperor Rudolf II in Prague.

Large exhibitions of European bronzes are extremely rare; one devoted to a single artist even more so. Although a few museums have been examining their European bronzes in a more or less systematic way, the relatively small number of well provenanced sculptures by any one artist in these collections means that our resource of comparative data for studying the techniques and materials of a particular artist or workshop is limited. The exhibition presented the unusual opportunity of having a large number of bronzes by a single artist together in one place at the same time-the chance to examine a variety of bronzes from throughout a single artist's career, systematically and under uniform conditions.

2. Organization of the Study

Three goals were set at the beginning of the project. The first was to understand as fully as possible all aspects of de Vries' working techniques. Before the exhibition opened, Dr. Francesca Bewer, Associate Curator of Research at the Harvard University Art Museums had been

contracted by the Rijksmuseum to carry out examinations of a number of the bronzes at their home institutions in order to prepare technical notes and an essay for the exhibition catalogue [2]. Although some of the exams were quite thorough, access to analytical equipment was limited in many instances. The initial survey provided an outline of the sculptor's technique, yet raised many important questions. Many of these questions could only be answered through systematic examination including, most importantly, x-ray radiography. The second project goal was to clarify attribution questions posed by some of the bronzes. The hope was that by more fully understanding the materials that de Vries used, as well as the methods he used for building his models and casting his bronzes, it would be possible to clarify the attribution of some of the works. The final goal of the project was to disseminate the information gathered during the study. It was hoped that as the project progressed, an appropriate format and venue would become apparent.

It was clear from the beginning that the time available for the exams would be extremely limited as the loan period could not be extended. Of the thirty-eight bronzes attributed to de Vries in the show, ten had already undergone thorough technical examinations, including bronzes from the Metropolitan Museum of Art in New York, the Nationalmuseum in Stockholm, The J. Paul Getty Museum in Los Angeles, and Lambach Abbey in Lambach, Austria. The remaining bronzes were prioritized based on those we knew the least about technically and on the art historical value of performing the exams. For instance, a very high art historical value was placed on any information that could be gained from comparing the technical details of the two Cain and Abel groups- the only signed compositions of which there are two versions [3]. Permission to carry out the exams was requested directly of the couriers. Without exception, each lending institution that was asked for permission agreed to the exams; in most cases the couriers themselves signed the permission forms. We found it advantageous to be able to explain the examination procedure in person, showing the facilities and describing the steps that would taken. In the end, 26 bronzes were examined: 10 were signed and dated, 9 were not signed but were attributed to de Vries, 2 were believed to have been cast from de Vries models, and 5 were aftercasts or works by other artists included in the show for comparison reasons. A full list of the bronzes included in the examination can be found in Fig. 3.

The technical study of Renaissance and later bronzes began at the Getty in the 1980's with the encouragement of the former Curator of Sculpture, Peter Fusco. In 1992, Francesca Bewer was hired to develop an examination protocol and to carry out a detailed technical study of over 40 of the Getty's European bronze sculptures [4]. The examination form developed at that time was adapted for the de Vries technical exams and was used for the examination of each bronze. The form is included as Fig. 4.

The examinations were carried out during the installation and deinstallation of the exhibition and during off-hours when the museum was closed, including early mornings and closed Mondays. The work was coordinated by the author with assistance throughout by Laramie Hickey-Friedman, Graduate Intern in Decorative Arts and Sculpture Conservation.

Each bronze was studied in phases including:

1. Interior and core. The large bronzes were examined while slung for installation or deinstallation; smaller bronzes were generally deinstalled and examined on Mondays when the museum is closed.

2. XRF and X-ray radiography. The analytical facilities are located in the Museum Research Laboratories of the Getty Conservation Institute. The large bronzes were examined during deinstallation immediately before crating. The smaller bronzes were generally taken to the analytical facilities on Mondays.

3. Visual exam of the exterior. Portable lights and a binocular microscope were kept in a closet adjacent to the exhibition gallery and were used for surface examinations during off-hours. Measurements were taken with a cloth tape, calipers, and wooden right-angle measuring sticks.

3. The Technical Study

3.1 Core Material

Many of the bronzes are open at the bottom, allowing for examination of the hollow interiors. Even when core and armature had been removed, more than sufficient core always remained in the recesses to yield a sample. Two core samples were removed whenever possible, one for petrographic and microchemical examination, and a second sample for thermoluminescence (TL) dating.

3.2 Petrographic and Microchemical analysis

Petrographic and microchemical analysis of the cores was undertaken in order to determine if de Vries was consistent in the materials that he used for making his cores, and to see if we could determine how his core materials were prepared. It was also hoped that a characterization of "typical" de Vries cores would further the attribution studies of some of the bronzes.

Ron Schmidtling, a consulting geologist to the Getty Conservation Institute, carried out the core analysis. Small core samples were prepared for petrographic analysis by mounting and polishing to 0.03 mm thickness. Components in the samples were then identified using the polarizing microscope. The relative amounts of each component were determined by the analysis of 200 random sites under 400x magnification. The quartz and feldspar grains were measured for mean average grain size and were examined for degree of angularity. The presence of calcite or gypsum was confirmed using microchemical tests. Finally, the cores were recorded with one photomicrograph of the powdered sample before preparation at 10x, and two photomicrographs

of the thin sections, one in transmitted light and one under crossed polars, both at 100x.

3.3 Thermoluminescence Dating

Thermoluminescence dating was undertaken for two reasons. The first was to help date the objects for which the date was uncertain, as one component in the attempt to determine whether or not they were modelled or cast by de Vries. The second reason was to understand more about the use of thermoluminescence dating for European casting cores. The Decorative Art and Sculpture Conservation laboratory has long used TL as an aid in the authentication of fired materials. The technique is complex and does not always yield clear results for European sculpture. The de Vries project presented an ideal opportunity for studying the usefulness of the technique for European casting cores. The sculptures presented three distinct groups: 1) signed and dated by de Vries 2) cast by de Vries at an unknown date 3) artist and date uncertain. Core samples from the first two groups were used for studying the accuracy of the technique. When calculating a date for relatively recent material, there will always be unknown quantities in the equation, leading to a degree of uncertainty expressed as $a \pm range$ in the results. In addition, the results from the TL lab which we generally use are reported with a standard deviation of one in which there is a 66% chance that the true date falls within the stated range. The dated bronzes and those long thought to have been cast during de Vries' lifetime were used to compare these calculated results to the known dates.

Whenever possible, at least 200 mg of core were removed for TL dating. The samples were either drilled out under safelight, or chunks of core were removed under ambient lighting conditions, to be further sampled later under proper lighting conditions by the TL lab. Some of the bronzes in the technical study did not contain enough core to warrant sampling. Samples of eighteen bronzes were sent to the Rathgen-Forschungslabor in Berlin. The analysis was undertaken by Ana Manzano under the direction of Dr. Christian Goedicke. A written report was prepared for each bronze that includes a table of measured quantities such as the accumulated dose, the alpha-count rate, and the potassium content. The report also gives details of the experimental procedure and the instruments used.

3.4 X-Radiography

X-ray radiographs were taken of the bronzes to allow a better understanding of their structures (Fig. 2). Francesca Bewer visited the museum twice during the exhibition to help with the interpretation of the radiographs. In all cases, the radiographs were taken after the interiors had been examined and core had been removed for thermoluminescence dating. Radiographs were taken with a Phillips 450 kV tube using Kodak Industrex M film in cassette holders with lead sheet measuring 0.01" in front of and 0.005" behind the film. The most descriptive radiographs were then digitized (grayscale at 304.8 DPI, file size approx. 50 MB), printed and annotated.

The high kV tube allowed penetration of the thicker sculptures that had not been successfully radiographed in the past. For example, in order to produce a good radiograph, it was necessary to shoot the torso sections of the Laocoon from the Nationalmuseum, Stockholm at 400 kV and 10 mA for three and a half minutes at a distance of 1.1 meters.

Positioning the x-ray film in the lead-lined cassettes behind the larger sculptures posed a challenge that was solved by constructing a film holder using tripod parts manufactured for photographers by Bogen Manfrotto. A tripod formed the main support, onto which a 24" horizontal arm was attached. A Bogen clamp on a swivel head was then attached to the arm. The clamp held a custom built u-shaped frame made of tubing onto which a sheet of aluminum was attached. The x-ray film cassette was then strapped to the aluminum sheet, and could be positioned at any angle at a height of approximately 16" to 70" from the floor. Photographer's lead weights were used at the base to keep the tripod from tipping.

3.5 Analysis of the Metal

Semi-quantitative x-ray fluorescence (XRF) was used to determine alloy content. XRF was chosen because it was available, and because it is non-destructive. Since samples do not need to be taken, it was possible to analyze the surface in numerous areas, including separately cast sections, cast-in repairs, plugs, and solder metal. XRF was done after the bronzes had been radiographed because the images indicated the location of features sometimes hidden on the surface. The analysis was undertaken using a Kevex instrument at 50 kV, 3.3mA, with a Ba/Sr secondary target and collimators of 3mm on the x-ray tube and 4mm on the detector with a 200 second acquisition time. The results were normalized to 100% by weight.

4. Results of the Study

The examination protocol developed for the Renaissance Bronze Project and adapted for this study has proven to be a thorough, viable method for examining European bronzes. The numerous categories in the examination form offer a consistent structure for the examination, yet the narrative format allows room for detailed descriptions where appropriate.

The technical study has told us much about the working techniques and materials used by Adriaen de Vries. In some cases, the data confirmed the earlier study done for the catalogue. In many instances though, new nuances were brought to light. The examinations have also furthered the attribution studies for one group of the bronzes.

The gathering of data for the technical study of the 26 bronzes was undertaken part-time during the run of the exhibition. Once permission for the exams had been acquired, the time taken for this aspect of the project was not overbearing. By far the most time-consuming aspect has been

writing the final reports. This has included following through with the analytical results, including such things as: proofing and revising the core reports; additional research into the TL results; and interpretation of the XRF results. In some cases, time has been spent researching the background of individual pieces including their original commissions or their collection history. Finally, in the closing "Conclusions and Comparative Analysis" section, an attempt has been made to compare or contrast each bronze technically to other pieces in the artist's oeuvre.

I feel that the project has been a great success, however one important aspect is as yet incomplete. The final, and ultimately the most important, step of the technical study will be the dissemination of the results. Each of the lending institutions has received a report on their bronze or bronzes, but all of the data should become available for broader use. At present, my hopes are riding on a proposal that has been submitted for publication of the individual reports accompanied by a small number of essays.

5. Conclusion

When an institution mounts a large exhibition of works of art, bringing them from around the world - always at potential risk to each object - it is necessary to step back and assess the goals of the exhibition. These goals will of course vary, but an important one is often to further scholarly research. Yet the scholarship relating to an exhibition is generally done before the opening in the form of a catalogue. During the exhibition itself, visitors gain an increased visual appreciation or understanding of an artist but no record of this aspect of the exhibition is created. In carrying out technical examinations of many of the bronzes while together on loan, we have made an important addition to the body of knowledge on the artist. It is hoped that in the future, technical studies may be considered a requisite to mounting a successful exhibition. In most cases, examinations as detailed as those undertaken for the de Vries exhibition will not be appropriate, yet steps as straight-forward as recording the conservator's visual observations in comparing and contrasting the works will add much to the legacy left behind once an exhibition closes.

It is hoped that this brief report of the logistics of the project can be of use to another institution at some other time, contemplating such an undertaking. We found that the lenders were grateful to receive the technical reports on their bronzes, suggesting that in the future institutions may consider the prospect of such studies a compelling reason to lend to exhibitions where such examinations are planned.

Acknowledgments

This project could not have been carried out without the help of Laramie Hickey-Friedman who offered keen insight in describing the bronzes, lasted through many long days of x-radiography, and oversaw the XRF analysis and alloy data management for each sculpture. I would also like to

thank my colleagues in Decorative Arts and Sculpture Conservation for their constant support during the exams and afterwards as the reports were written. I am grateful to Kevin Marshall and to all of the museum Preparators for their good-natured help and patience in allowing us the time and opportunities to safely carry out the exams. I am indebted to Peter Fusco, Peggy Fogelman, Francesca Bewer, David Scott, and Brian Considine for their open spirit of shared scholarship and collaboration, as well as their unwavering support of my continuing this work.

Endnotes

1. The exhibition was organized by Frits Scholten, Curator of Sculpture at the Rijksmuseum, Amsterdam. The exhibition dates were as follows: Amsterdam Dec. 12, 1998 through March 14, 1999; Nationalmuseum, Stockholm April 15 through August 29, 1999; The J. Paul Getty Museum, Los Angeles October 12, 1999 through January 9, 2000.

2. Scholten, F, ed. 1998. Adriaen de Vries (1556-1626): Imperial sculptor. Amsterdam: Rijksmuseum.

3. One resides in The Torrie Collection, The University of Edinburgh, inventory #49. The second resides in the Statens Museum for Kunst, Copenhagen, inventory #5492.

4. Referred to as The Renaissance Bronze Project, each of the Getty bronzes was examined using a form similar to that discussed in this paper. The data has not yet been published but individual inquiries from other institutions for the purpose of comparison are welcome.

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Figure 1. The exhibition Adriaen de Vries: Imperial Sculptor installed at The J. Paul Getty Museum.



Figure 2. Laramie Hickey-Friedman in the x-ray radiography lab with *Psyche Borne Aloft by Putti* from the Nationalmuseum, Stockholm. Note the tripod adapted to hold the film cassette.

TITLE	ATTRIBUTION	INSTITUTION/CITY
Psyche Borne Aloft by Putti	Adriaen de Vries	Nationalmuseum, Stockholm
Nymph and Dancing Faun	Adriaen de Vries	Staatliche Kunstsammlungen Dresden,
	(model)	Dresden
Crucifix .	Adriaen de Vries	Parochierk, Wullenstetten
Venus or Nymph	Adriaen de Vries	Herzog Anton-Ulrich Museum,
	(model)	Braunschweig
Sextus Tarquinius	Adriaen de Vries	private collection, London
Threatening Lucretia	(model)	
Portrait of Emperor Rudolf II	Adriaen de Vries (signed and dated)	Kunsthistorisches Museum, Vienna
Hercules, Nessus and	Adriaen de Vries	Louvre, Paris
Deianeira		
Hercules, Nessus and	Charles Crozatier	Rijksmuseum, Amsterdam
Deianeira	(1795 – 1855)	
Hercules, Nessus and	Charles Crozatier	Nelson Atkins Museum, Kansas City
Deianeira	(1795 – 1855)	
Allegory of the War Against	Adriaen de Vries	Kunsthistorisches Museum, Vienna
the Turks in Hungary	(signed and dated)	
Horse	Adriaen de Vries	Národní Galerie v Praze, Prague
X 1 X D	(signed and dated)	
vulcan's Forge	Adriaen de Vries	Bayerisches Nationalmuseum, Munich
Cain and Abel	Adriaen de Vries	The University of Edinburgh Edinburgh
	(signed and dated)	
Flora	Adriaen de Vries	Museum der bildenden Künste, Leipzig
Farnese Bull	Adriaen de Vries	Schlossmuseum, Gotha
	(signed and dated)	
Christ at the Column	Adriaen de Vries	Kunsthistorisches Museum, Vienna
Lazarus	Adriaen de Vries	Statens Museum for Kunst, Copenhagen
Dette mithe C	(signed and dated)	
Putto with a Goose	Adriaen de Vries	Nationalmuseum, Stockholm
	Adriaen de Vries (signed and dated)	Statens Museum for Kunst, Copenhagen
Laocoon and His Sons	Adriaen de Vries (signed and dated)	Nationalmuseum, Stockholm
Hercules Pomarius	Adriaen de Vries	Muzeum Hlavního Mesta Prahy, Prague
Bust of Christian II	Adriaen de Vries (signed and dated)	Staatliche Kunstsammlungen, Dresden
Flying Mercury	Pietro Francavilla (1553 – 1615)	Norton Simon Museum, Los Angeles
Mercury & Psyche	School of Adriaen	Huntington Art Gallery, San Marino
	de Vries	
Mercury	Williem Tetrode (ca. 1525 - ca. 1588)	Los Angeles County Museum of Art
Christ Mocked	17 th C.Italo-Flemish	Los Angeles County Museum of Art

Figure 3. Bronzes examined at the J. Paul Getty Museum during the exhibition Adriaen de Vries: Imperial Sculptor

Figure 4. Examination form used during the study

The J. Paul Getty Museum Decorative Arts and Sculpture Conservation

BRONZE EXAMINATION REPORT

Title: Artist: Lender: Lender's Inv, #: Exhibition Catalogue #: Date: Dimensions: H.: cm x W.: cm x D.: cm Marks and Inscriptions:

Summary Description:



EXAMINATION

1. Mount

2. Alloy

- 3. Evidence of the technique of fabrication
 - a. Internal metal armature and core supports
 - b. Core pins
 - c. Core material
 - d. Internal surface of the bronze
 - e. Method of assembly and joining of individual wax or cast bronze components
 - f. External surface of the bronze: evidence of the wax model and of final surface chasing
 - g. Surface Coatings
- 4. Casting defects and foundry repairs
- 5. Later modifications/restorations

* * *

CONCLUSIONS AND COMPARATIVE ANALYSIS

NON-DESTRUCTIVE DECONSTRUCTION OF THE LIDOW FANG HU ON PEDESTAL

Laramie Hickey-Friedman

1. Introduction

From 1998-2001 technical studies were conducted on many of the Chinese bronzes in the permanent collection at the Los Angeles County Museum of Art, including the Lidow fang hu, a Chinese cast-bronze from the Late Eastern Chou period (acc. No. 78.123a,b). The study was initially undertaken to answer curatorial questions regarding the extent of previous restoration campaigns and methods of fabrication. The interest in the examination of this piece was coupled with a larger study of the materials and techniques used for the restoration of Chinese bronzes. Detailed examination and analysis of the heavily restored fang hu brought forward questions regarding its historical interpretation. In consultation with the Curator of Chinese and Korean Art, available information was pooled to gain a cohesive historical understanding of LACMA's Lidow fang hu, and attempt to characterize the restoration methodology.

As part of a larger study of our Chinese bronzes, initially this piece was brought into the lab to resolve questions from the Far East Asian department. The curator, Keith Wilson, wanted to know if the vessel and pedestal were cast integrally and if the pedestal was originally designed to detach from the vessel.

The LACMA fang hu was published on its own merit as an important footed vessel. The Waterbury publication (1952), followed by that of Weber (1967), gave the fang hu a solid provenance based primarily on the design motifs, and their relation to other pieces with similar motifs.

Included is a brief introduction to the Lidow Collection at LACMA and the history of the fang hu, followed by known restoration techniques used on ancient Chinese bronzes, as it relates to this study. The results of examination, which include x-ray radiography and metallography, are also described.

A review of the known history, from curatorial files, publications, and excavation reports was conducted in order to answer the curator's questions, and have a better understanding of this piece. It should be noted that when this piece was donated to LACMA, the current curator did not ask for receipts or documents pertaining to this piece. Hence, some of the object's history is sketchy and it was felt the best way to unfold its past was through a deconstruction process.

2. History

Prior to accession in 1978, the fang hu belonged to Mr. Eric Lidow, a well known collector of ancient Chinese bronzes. A published catalogue (LaPlante 1958) shows the fang hu belonging to Mr. Lidow in 1958. In 1952 this piece was published and the current owner identified as Mr. Scott Tsuchiya, a collector from San Francisco (waterbury 1952). There are no other historical references or publications of this piece other than the excavation records.

According to the published excavation report (Institute of Archaeology, Academia Sinica 1938), the object went to the Academia Sinica in Taiwan in 1937. The archaeologist stayed in China, and wrote his excavation report based entirely on his notes and rubbings.

This object was excavated between December 1935 and sometime in 1937 from the late Chou site of Liulige, near the town of Hui Xian, in the Henan Province [1]. The outbreak of war with the Japanese in 1937 ended official excavations. Excavation records and illustrative rubbings provide evidence that a similar piece (with a different base) exists/ed in Taiwan. Excavation records state that the pedestal (described as the stem of a dou) was found in tomb 75, and the vessel (described as a hu) was found in an adjacent tomb, 76. The excavator identified the remains in tomb 76 as those of a woman, implying that the two tombs were that of husband and wife. The reports do not indicate that the vessel fragments and the pedestal are in any way related (Institute of Archaeology, Academia Sinica 1938).

3. Technical Examination

From a technical standpoint mold lines are clearly visible on the vessel and pedestal, down to the flared base. The mold lines on the vessel do not correspond to the pedestal, and there are no mold marks on the flared base. The incised decoration on the vessel and the pedestal appear to have been made in the model rather than in the mold, typical of ancient Chinese bronze manufacturing techniques (Fig. 1).

A closer look revealed that the vessel was not centered on the pedestal, and there were fills around the join of the vessel to the pedestal. While it was clear from surface magnification and general examination that the object was restored, the extent of restoration was uncertain, prompting x-ray radiography (Fig. 2).

X-Ray radiography confirmed extensive restoration on the vessel and pedestal. The lower section of the vessel appeared to be mostly reconstructed with a wire mesh support and fill material. Additionally interesting detail was apparent on the lower portion of the pedestal. A modern replacement had been added to the base of the stem, attached with a screw. The x-rays also showed two pins inserted in the original part of the stem (Figs. 3 and 4). Interestingly, there was very little evidence of lead metal, as lead solder is a common material found in Chinese bronze

restoration (Gettens 1969).

A sample for metallography was removed from the base to confirm it was a modern replacement. There is a clear frontier of corrosion to the alpha phase, leaving the alpha plus delta eutectoid relatively unharmed. This type of selective corrosion plus large bright red/orange cuprite crystals are indicative of a newer corrosion product. Additionally, lead inclusions in the alloy are mainly intact. It is quite possible that this type of corrosion was formed with a combination of heat and chemical patination. No other samples were removed from the object (Figs. 5 and 6).

4. Comparison

The next step was to compare the fragment rubbing from the archaeologist's report to the LACMA fang hu. A comparison of losses to those exhibited in the rubbing was conducted, but a matching profile on the LACMA piece was not evident. The design elements on both the rubbings and the vessel are very similar. The pedestal showed the same design characteristics as the rubbing. However, the rubbing also had a flared base that is different from the LACMA fang hu. The design elements on the base are a unique puttiesque bird-man figure, and the rubbings have a bird motif (Figs. 7, 8, and 9).

5. Discussion

The examination was able to address the curator's initial questions. It is unlikely that the pedestal and the vessel were cast together. There is no definitive evidence to explain how the pedestal originally joined the vessel, or if it was ever joined. The form of a hu or fang hu on a pedestal, while not common, does exist in both ceramic and bronze vessels. The curator's research suggested that this was a later more creative form concurrent with the Late Chou fanciful animalistic forms. The cover of *Orientations* (December 1989) featured a pair of recently excavated fang hu on pedestals. Other publications have also represented this type of vessel in pairs (Pope :449-500; Fang-mei :321). This does give evidence that LACMA's fang hu is perhaps one of a pair, and that the mate (or separated vessel and pedestal) is located at the Academia Sinica.

While the original questions were satisfied, more questions surrounding the fang hu came to the surface. There is no clear evidence besides previous publication that the pedestal and vessel were made to be one object. As only a handful of these forms are known, the majority in China, the authenticity of LACMA's fang hu (or more precisely, its form) was questioned. What was the intent of the restorations? Was it a harmless but ill-conceived joining by the Academia Sinica in Taiwan, or was this a successful attempt by a dealer to make a duplicitous but more valuable fang hu on a pedestal? The larger dilemma for conservation was whether or not to deconstruct the fang hu, and attempt to re-assemble the fragments.

At this point, it is important to clarify that restorations on Chinese bronzes are not unusual. While many pieces are in pristine condition, there are also many that have undergone some alteration. In LACMA's collection alone there are examples where the entire object is reconstructed of fragments or later additions made to the form (Fig. 10).

It is not unusual for the conservation treatment of pastiches to lead to more pieces than originally existed. Often, once the fill materials are removed and the fragments cleaned of excess residue there are no cohesive join or break edges to justify reconstruction. One must truly consider the treatment before proceeding to the point of no return.

6. Conclusion

This deconstruction yielded interesting information regarding both the history and the reconstruction of this fang hu. The publications referenced were useful for establishing precedence for the existence of this form. While later publications show the fang hu in its current state, the archaeological notes and rubbings do not support the joining of the vessel and the pedestal. However, the rubbings suggest a relation to fragments in the Academia Sinica.

Based on manufacturing techniques and visual examination of the corrosion products, the various fragments of the LACMA fang hu are authentic Late Chou Dynasty, with the exception of the flared base. Additionally the vessel and pedestal are not cast integrally. Finally, since there is no clear evidence to suggest a method of joining the two, reversal of the restoration is not warranted at this time.

Acknowledgements

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Additionally these institutions graciously allowed access to their Chinese bronze collections for comparison and examination. Freer Gallery of Art, Metropolitan Museum of Art, Museum of Fine Arts- Boston, Art Institute of Chicago, Cleveland Museum of Art, Fogg Art Museum, British Museum, Rijksmuseum

Endnote

1. During the Late Chou period, the town was under control of the State of Wei, which was

different from the State of Wei during the Early Chou period. During the Warring states period, the royal capital was located at Louyang, but there was no cohesive government at the time.

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Figure 1. Mold lines highlighted on vessel and pedestal.



Figure 2. Detail of restoration at the base of the vessel.



Figure 3. X-ray radiography of the vessel. The circled area indicates the lower section of the vessel that is mostly reconstructed with wire mesh support and fill material.

Figure 4. X-ray radiography of the stem. The top arrow shows the area of unusual density at the join between the vessel and stem. The bottom arrow indicates two pins inserted in the original part of the stem.



Figure 5. Metallography sample, bright field. The corrosion layer, identified by dark voids, appears at the top of the image. This is where the copper-rich alpha phase was attacked. There are dark globules of lead within the matrix which would not be expected in a metallographic sample of an ancient bronze.



Figure 6. Metallography sample, dark field. The corrosion layer appears at the top of the image. There is a top layer of carbonates (green in the original photograph) and a frontier layer of cuprite (red/orange in the original photograph) beneath.

Hickey-Friedman



Figure 8. Overlay of the rubbing on the LACMA fang hu.

Figure 7. Archaeological rubbing of the stem (Academica Sinica 1938)



Figure 9. Archaeological rubbing of the vessel (Institute of Archaeology, Academia Sinica 1938).



Figure 10. X-ray radiography of a reconstructed fang yi. (Los Angeles Count Museum of Art, acc. no. AC.1998.251.35a,b)

IMAGE RECOVERY OF WORN-OFF HALLMARKS ON SILVER AND GOLD OBJECTS

Paul L. Benson and Robert S. Gilmore

1. Introduction

The use of hallmarks on silver has a long history dating back to the fourth century AD and represents the oldest known form of consumer protection. A series or system of five marks has been found on Byzantine silver dating from this period though their interpretation is still not completely resolved (Dodd, 1961).

Hallmarking of European silver probably originated in France in the 13th century and spread from there to other countries. The first hallmarks represented a guarantee of the silver or gold content of the metal alloy or their place of manufacture. For example, the alloy that is today universally recognized as 'sterling silver' (92.5% silver) originated in an English statute of 1300 and was based on the alloy of the English silver coinage in use at that time. The English gold alloy standard was based on an existing alloy standard known as the "touch of Paris" or 19.2 carats/ 80% gold (Hare, 1978). In contrast to these long established standards the American standards were not formalized until 1906.

Over time, additional hallmarks were placed on silver and gold objects to denote various aspects of the manufacturing process such as the maker's name, the location of the assay office where the alloy was tested, the year of manufacture, tax implications, and commemorative events (Fig.1).

As hallmarks were a form of consumer protection there were strict penalties for their misuse. For example, a metalsmith could have his substandard wares seized, he could be fined, jailed, maimed, banished, or even put to death (Jackson 1921).

The history of European hallmarking of silver and gold is far from complete as some historical records have been lost through time. For example, the London guildhall records prior to 1681 were lost in a fire at the Assay Office and, in Holland, records were destroyed when the guild system was abolished in 1807. As the history and standards of hallmarking silver and gold objects from various countries is complex, it should be consulted on an individual basis (Wyler, 1937; Jackson, 1921).



Figure 1. Typical set of English hallmarks indicating that the object is made of sterling quality silver, made by Hester Bateman in London in the year 1787, and that a duty has been paid on the piece.

Hallmarks on silver and gold objects can fix these pieces in history by providing direct evidence of the maker, the place and date of manufacture, and the quality of the metal alloy at a particular time. To some extent then, the historic, monetary, and intrinsic value of the objects are directly linked to the ability to discern the hallmarks. The susceptibility of silver to tarnishing means that it must to be polished regularly to maintain its desired bright metallic surface finish. The polishing process removes a thin layer of silver metal so that over time the hallmarks will be gradually reduced to the point where they are either illegible or completely worn away, resulting in the loss of valuable historic information. The ability to read the original marks would greatly aid in placing these objects back into their rightful place in history.

Even though the hallmark can be completely worn away there may still be remnant plastic deformation within the metal from the act of striking the surface to create the hallmark. This residual deformation can be characterized in the form of an acoustic response when the surface is insonified with a focused acoustic beam; the amplitude of the response is then used to create an image on a computer screen. A highly polished metal surface provides a nearly ideal medium for the utilization of acoustic imaging techniques.

Other methods have been successfully employed to image worn-off information from metal. For

example, recovery of filed-off serial numbers from firearms is a well-established procedure in law enforcement forensic laboratories (Fig. 2).

METHODS OF RECOVERING OBLITERATED SERIAL NUMBERS FROM FIREARMS
Chemical and Electrolytic Methods- etching by chemical or electrolytic process
Acid Etching- Fry's reagent, nitric acid, ferric chloride, Restora-A-Gel
Electro polishing
Electro etching with a DC current
Ultrasonic Cavitation- etching by action of water in state of cavitation
Dental De-Scaler
Magnetic Particle Method- application of magnetic particles to magnetized specimen
Magnaflux
Heat Treatment Methods- gradual heating of metal surface
Heat Tinting
Heat Etching
Cold-Frost Method- application of extreme cold to produce frost on the surface
Dry Ice
Radiography
X-rays and Gamma rays
Liquid Penetrant Method- application of a liquid and a fluorescing developer
Crack Location
Electroplating- application of a metallic coating on the surface Copper or nickel plating

Figure 2. Various methods that have been proposed to recover obliterated serial numbers from firearms (after Treptow 1978).

Unfortunately, most of these techniques are destructive to the metal to some extent. The most common technique involves polishing the area to be imaged and then etching the surface with an acid to bring out the latent serial numbers; needless to say, the use of this technique would not be tolerated on works of art. The newly developed acoustic imaging procedure is non-contact and does not harm the metal in any way. It is the only known non-destructive technique that has the potential to recover lost information from silver, gold, and other metallic works of art.

2. Ultrasonic Imaging Systems and Scanning Acoustic Microscopes

2.1 History

The ultrasonic imaging technologies for visualizing the surfaces and interiors of opaque solids are well established (Gilmore, 1999). Between 1929 and 1931, Sokolov and Mulhauser independently proposed the use of ultrasonic waves to form images of the interior of materials for materials characterization and non-destructive evaluation (NDE). During the 1930s efforts to develop ultrasonic images involved the development of acoustic amplitude sensitive screens that displayed visible contrast in proportion to the acoustic amplitude incident on the screen. These image converter screens (such as the Pohlmann Cell and the Sokolov Tube) had such poor sensitivity and resolution that little use was made of them other than as curiosities. Pulse-echo and pulse-transmission C-Scan images, using both focussed and unfocused ultrasonic beams, were introduced in the early 1950s. The primary use was for industrial NDE.

These initial C-Scan images were displayed on photographic or voltage sensitive paper and were acquired by scanning a single transducer back and forth over the subject material. The image was built up line by line. By the early 1970s ultrasonic C-Scan inspections of both the surfaces and interior volumes of industrial materials were in general use and C-Scan images had been produced as high as 50 MHz in frequency. In the early 1970s work at Stanford University under the direction of C. F. Quate (Lemons and Quate, 1979) combined zinc oxide on sapphire transducers, C-Scan data acquisition, and microwave electronics to create very small ultrasonic images at GHz frequencies. These images rivalled optical microscopy in resolution, detail, and field of view; therefore, the devices that made them were called Scanning Acoustic Microscopes. The GHz frequencies, low depths of penetration, and very small fields of view limited the industrial usefulness of scanning acoustic microscopy except for microelectronic assemblies. However, the near optical resolution of the acoustic microscope images provided a new emphasis and enthusiasm for ultrasonic imaging in general. This renewed effort combined with the collateral advances in the computational power, storage, and display capabilities of small computers resulted in three decades of rapid progress in ultrasonic imaging devices, methods and applications.

By the start of the 21st century ultrasonic imaging methods were well established to characterize material microstructures, bonds, defects (flaws, voids, cracking, porosity, layer delaminations), coating delaminations, elastic modulus and density variations, heat-affected zones in welds and other fusion processes, stress distributions in isotropic materials, and in vitro carious lesions.

Materials examined include ceramics, composites, glass, metals and alloys, polymers, plastics, semiconductors, electronic components, geological materials, coffee and soybeans, bone, teeth, soft biological tissue, and organic compounds. However, a literature search has found only three references to acoustic microscopy and metal or ceramic art objects (Stravoudis, 1989; Benson, 1991; Ouahman, 1995).

2.2 Description of the Acoustic Microscope

Several texts are available that clearly describe ultrasonic imaging and acoustic microscopy (Lemons and Quate, 1979; Briggs, 1982; Gilmore, 1999); therefore, the characteristics and operation of the systems will only be summarized here. A typical transducer used for acoustic imaging consists of a piezoelectric layer cut to a specified frequency and bonded to a planoconcave lens to focus the ultrasonic beam. For high frequency operation the lens is usually fabricated from single crystal sapphire or fused quartz. Alternatively, eliminating the lens and spherically curving the piezoelectric layer itself can also focus the ultrasonic beam. In the case of pulse-echo C-Scan data acquisition, the transducer acts as both the transmitter and receiver of the acoustic energy. A short electrical pulse is applied to the piezoelectric layer to create the acoustic pulse and return acoustic echoes interact with the layer to create electrical signals. The object to be scanned is placed at the focal point of the ultrasonic beam. What makes an acoustic microscope unique is the ability to place the focal point of the acoustic energy either on the surface of the object or subsurface in the object's interior. Again, as with all C-Scan type data acquisition, the image is acquired by raster scanning the ultrasonic beam and acquiring echo amplitudes at an increment along the scan lines equal to the line-to-line spacing (Fig. 3).





2.3 Coupling Fluid

For frequencies much above 1 MHz, acoustic waves are rapidly attenuated in air so it is necessary to utilize a coupling fluid between the transducer and object to be imaged. The acoustic properties of the coupling fluid are a significant factor in determining the resolution that can be achieved by the acoustic imaging system. The most widely used fluid is water but other fluids have acoustic properties (namely a higher or lower velocity) that make them superior to water particularly when surface wave imaging is used (Table 1).

COUPLER	TEMPERATURE	VELOCITY	ABSORPTION	COEFFICIENT
Water	25	1495	22.0	1.0
Water	60	1550	10.2	1.4
Acetone	30	1158	54.0	0.8
Ethanol	30	1127	48.5	0.8
Methanol	30	1088	30.2	1.1
FC-40	25	656	Not available	Not available
(table is mod	lified after Lemons and Q	uate, 1979)		

Table 1. Relative Acoustic Velocities of Some Coupling Media

For this work Fluorinert FC-40 (an inert and environmentally friendly fluorocarbon fluid with a velocity less than half that of water) was used to make surface wave images in the sterling silver and gold objects discussed here. Usually, the object is submerged in the fluid while being scanned but some systems use pumped fluid columns essentially squirted at the surface being scanned. The images acquired in this work were all made by immersing the objects in FC-40 or water.

2.4 Acoustic Transducer

The choice of the coupling fluid was also based on how surface waves are produced in water versus FC-40 and the availability of existing acoustic transducers. When using water as a coupling fluid the angle of incidence needed to generate surface waves in silver is greater than 65° and transducers with this geometry would have to be custom-made. By using the FC-40 with its slower acoustic properties the angle of incidence needed to generate surface waves in silver is approximately 24° and 29°-35° in gold. Transducers with these geometries are readily available (Table 2). Note that it is not possible to generate surface waves in gold using water as the coupling fluid as the angle of incidence is greater than 90°.

	Sterling Silver	18K Go	old 22K	Water	FC-40
Longitudinal velocity	3.89 mm/sec	3.55 mm/sec	3.39 mm/sec	1.48	0.656
Shear velocity	1.73	1.46	1.31	0	0
Rayleigh velocity	1.63	1.33	1.15	Frequency dependent	Frequency dependent
Angle of	$FC-40 = 23.7^{\circ}$	$FC-40 = 29^{\circ}$	$FC-40 = 35^{\circ}$		
generate surface waves	Water = 65.3°	Water = >90°	Water = $>90^{\circ}$		

Table 2.	Acoustic Velocities and Angle of Incidence to Generate Surface	Waves in
	Sterling Silver and Gold	

Back-surface imaging was done at 50 MHz using a Panametrics type V390 F/2 transducer with a 1.5" diameter quartz buffer-rod and a 0.25" diameter beam focussed at 0.5" in water. Surface wave imaging was done at 20 MHz using a Panametrics F/1 polymer film transducer with a 0.4" diameter beam focussed at 0.4" in the FC-40.

3. Methods of Creating an Acoustic Image

The contrast changes in acoustic images are produced by variations of elasticity, density, and acoustic attenuation within the material to be imaged. In the specific case of imaging worn hallmarks, this paper will demonstrate that images of the residual deformation in the metal from the stamping process can be obtained by two methods: (1) Surface wave imaging of the surface containing the hallmark deformation (Fig. 4a), (2) Back-wall or back surface imaging where an acoustic beam is focussed through the full thickness of the metal and on the back surface containing the hallmark deformation (Fig. 4b). In other words, surface waves are used to produce images of the entry surface, i.e., the struck surface, where back-wall images are obtained from the surface opposite to the struck surface.



Figure 4. Schematic showing (a) back surface reflection imaging (or back-wall imaging) and (b) mode converted surface wave imaging.

4. Factors in Determining Suitability for Acoustic Imaging

4.1 Stress Annealing Temperatures

A first step in determining if residual deformation in silver or any other material is a candidate for acoustic imaging is to determine the stability of this deformation over time. The lowest temperature that might affect this stability is the residual stress annealing temperature. This is generally considered to be approximately 4/10ths (0.4) of the absolute melting temperature as expressed in degrees Kelvin (K) (Callister 2003). The highest temperature below the melting point affecting the retention of the deformation is less exact, but is the range in temperature at which recrystallization occurs. Here the grain boundaries in the silver migrate and the microstructure entirely recrystallizes. Any residual plastic flow remaining from a hallmark would begin to relax at the stress anneal temperature and could totally disappear during recrystallization. Since the melting point (Mp) of sterling silver is 893°C = 1166 K the stress anneal temperature would fall at approximately $0.4 \ge 1166 \text{ K} = 466 \text{ K}$ or approximately 93° C above the boiling point of water (100° C or 373 K). Room temperature is typically approximated at 300 K and since the lowest critical temperature for sterling silver (466 K) is well above this temperature, it seems reasonable to expect the residual deformation produced by a hallmark stamp to be relatively stable over a few hundred years of time, even if repeatedly washed in hot water. Stress annealing temperatures for other metals are shown in Table 3.

METAL		MELTING POINT (MP) IN DEG. CELSIUS	STRESS ANNEALING TEMPERATURE IN DEG. CELSIUS	RATIO OF MAX. AMBIENT TEMPERATURE TO MP IN DEG. KELVIN*
Gold	24K	1063	261	0.24
	22K	1003	237	0.25
	18K	905	198	0.27
	14K	845	173	0.28
Silver	pure	962	221	0.25
	sterling	863	193	0.27
Copper		1082	269	0.23
Lead		327	-33	0.50
Bronze	10% tin	1005	238	0.25
	20% tin	890	192	0.27
Brass	10% zinc	1040	252	0.24
	20% zinc	995	234	0.25
Iron		1538	451	0.18
Steel		1515	442	0.18

Table 3.	Stress	Annealing	Temperatures	for	Various	Metals
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*At ratios less than 0.40 the plastic flow surrounding the hallmarks should be stable at temperatures up to the stress annealing temperature

****** Gold alloy melting point data from Smith 1978; remaining melting point data from Lide 2002; all other figures have been calculated.

4.2 Anisotrophy

A second consideration in imaging residual deformation is to determine the acoustic properties of the subject material and any possible anisotrophy of the material. Unless the deformation process produces micro-fractures there is no reason to anticipate that a truly isotropic material would be rendered anisotropic by plastic deformation. Anisotropic materials, however, should undergo considerable change during deformation, since a local deformation would significantly rearrange

that microstructure. It seemed appropriate to estimate the anisotrophy in silver to determine if ultrasonic backscatter from the silver microstructure itself might be used to track the deformation underlying hallmarks. The three elastic constants for single crystal silver (cubic system) are C11 = 1.239 Mbar, C12 = 0.939 Mbar, and C44 = 0.461 Mbar (Simmons and Wang, 1971). Isotropic materials have only two independent elastic constants instead of the three required to describe the cubic system. A typical test for isotropy (again within the cubic system) is given by the Zener anisotrophy ratio of [C11 - C12] / 2.0 to C44 (Chung and Buessem 1968). Clearly 1.239 - 0.939 / 2.0 = 0.150 and is not equal to 0.461 so silver possesses considerable anisotrophy. Therefore, ultrasonic backscatter from the silver grains should be able to track the modifications in the microstructure caused by the plastic flow in the silver around the hallmarks. Anisotrophy for other metals are shown in Table 4.

METAL	C 11	C12	C44	RATIO OF C11-C12/2.0 TO C44*
Gold	1.923	1.631	0.420	0.15
Silver	1.240	0.937	0.461	0.15
Copper	1.684	1.214	0.755	0.24
Lead	0.495	0.423	0.149	0.05
Brass-4% zinc	1.633	1.177	0.744	0.23
9% zinc	1.571	1.137	0.723	0.22
17% zinc	1.499	1.098	0.715	0.20
Iron	2.314	1.346	1.164	0.49

Table 4. Estimation of Degree of Anisotrophy of Various Metals

*If this ratio is less than C44 then the metal exhibits anisotropy (from Chung and Buessem, 1968)

Having established this possibility one should immediately state that backscatter imaging of the silver microstructure has not proven effective to date for displaying residual deformation in the silver. The probable explanation for this has to due with the small size of the silver grains so that even at 50 MHz the grains are too small to provide any backscatter amplitude.

5. Experimentation

5.1 Sterling Silver Coupon

Initial experimentation was conducted on a blank sterling silver (92.5% silver) coupon measuring approximately 25 mm x 25 mm x 3 mm. An experienced silversmith then placed three different hallmarks on one surface. A silversmith was employed to produce the hallmarks

thinking that he would strike the silver with approximately the same force used by silversmiths for the past several hundred years so that the marks would be neither too deep nor too shallow. The struck surface of the coupon was polished with a Struers Prepamatic rotary lapping machine operating at thirty Newtons force at 150 RPMs counter-revolution. The lapping machine used a nine-micron diamond polishing abrasive compound to polish away the surface until the hallmark was no longer visible; approximately 0.3 mm of silver was removed. This was done to approximate the slow removal of the silver surface in much the same manner as years of polishing. Once the marks were completely removed from the surface the coupon was placed in a container with some keys and the container vibrated to produce scratches on the silver to simulate the surface on a genuine aged silver object. The three ultrasonic images shown in Fig. 5 illustrate the detail ultrasonic imaging can produce on both intact hallmarks and the deformation remaining after removal by polishing. Fig. 5a shows a 50 MHz F/2 back wall image of a coupon that still retains almost all of the hallmarks placed on it. Fig. 5b shows a 50 MHz F/2 back-wall image of the residual deformation in a similar coupon where almost all of the original hallmarks have been polished away. Fig. 5c shows a 20 MHz F/1 surface wave image of the same deformation in Fig. 5b except viewed from the surface containing the residual deformation. Both back-wall images were acquired using water to couple the ultrasonic beam into the part. The surface wave image used FC-40 in order to mode convert a longitudinal wave in the fluid into a surface wave on the silver coupon's surface.



Figure 5. Three ultrasonic images of the sterling silver coupons. (a) A 50 MHz F/2 back-wall image of the original hallmark. (b) A 50 MHz F/2 back-wall image of the residual deformation remaining in a similar coupon where the hallmark has been polished away. (c) A 20 MHz F/1 surface wave image of the same deformation in 4b except imaged from the surface containing the deformation.

5.2 Sterling Silver Spoon Handle

Fig. 6 shows a set of surface wave images of a sterling silver spoon wrought by Peter and Ann Bateman dating from 1792. This teaspoon, one from a set of eight, was chosen because its four hallmarks varied from perfectly readable to completely polished away. Also, the four hallmarks are legible on the other spoons from this set, making it easier to target the desired image quality. In Fig. 6a the makers' initials are clear but much of the remaining hallmarks have been removed. Fig. 6b shows the isolation, magnification, and partial recovery of one of the hallmarks believed to be that of a lion. The image of the "lion" shown in Fig. 6c is the best result of a series of trials where the focus of the transducer was changed slightly for each trial. The importance of even very small changes in the system focus has been repeatedly demonstrated in the course of this work. To the untrained eye the figure of the lion is not clear in the acoustic image but to an expert it is readily discernable (Wilkes, 2001).



Figure 6. (a) Ultrasonic images of the handle of a sterling silver teaspoon wrought by Peter and Ann Bateman dating from 1792. (b) The initials of the makers are clear but much of the remaining hallmarks have been removed. (c) Shows the isolation, magnification and partial recovery of a figure thought to be a lion. (Nelson-Atkins Museum of Art, No. 72-45/4B)

Subsequent image processing comparisons with a visible hallmark from a teaspoon from this same set of spoons has confirmed that the recovered image of the lion mark is identical to the visible hallmark. A series of six acoustic images of the worn-off lion hallmark were adjusted for size and overlaid on a digital image of the visible lion hallmark. The acoustic images were made by adjusting the focal spot of the sound waves either a little higher or a little lower in the metal. With only a two hundred nanosecond difference in the travel time of the sound waves from the first acoustic image to the sixth one there was a surprising difference in the quality of the images (200-nanosecond travel time converts to an actual distance difference of 0.0026 inch). The composite acoustic images had near perfect registration on the visible hallmark which demonstrates that the illegible hallmark was struck with the same die as the visible hallmark on the teaspoon from this set of teaspoons (Fig. 7).



Figure 7. A recovered acoustic image of a worn-off lion hallmark overlaying a digital image of an identical hallmark from the same set of teaspoons.

Fig. 8 shows the best results of a series of trials on recovering the date letter 'r'. Here, a series of three acoustic images of the letter 'r' were adjusted for size and orientation then overlain on top of a digital image of the corresponding hallmark from another teaspoon from the same set. Again, there is near perfect registration of the recovered acoustic image on the visible hallmark. This demonstrates that the recovered hallmark image is actually the letter 'r' and that it was struck with the same die as the visible hallmark on the other teaspoon.


Figure 8. Recovered acoustic images of the date letter 'r' overlaying a digital image of a visible 'r' hallmark from the same set of teaspoons.

5.3 Sterling Silver Fish Knife Blade

Fig. 9 is intended to show the lack of subsurface deformation where one would naturally assume that it should be present. Shown is a set of ultrasonic back-wall images of the sterling silver blade of a French fish knife dated approximately 1875 to 1925. One hallmark has been isolated and magnified (b) for comparison to the back-wall image of the deformation in the test coupon (c). Clearly no deformation appears to extend from the fish knife hallmark, suggesting that it has either been improperly struck by the silversmith, it has been worn away through the subsurface deformation zone, or the residual deformation has been 'relieved' during an annealing process. The annealing process could have occurred during manufacture, or the heat from the process of soldering the handle to the blade may have been sufficient to cause a localized annealing of the hallmarks since they are placed quite close to the attached handle.



Figure 9. Ultrasonic back-wall image of the sterling silver blade of a French fish knife dated approximately 1875 to 1925. One hallmark is isolated (b) and magnified for comparison to the back-wall image of the coupon (c). No deformation appears to extend from the fish knife hallmark. (Nelson-Atkins Museum of Art, no. F83-76/10)

A literature search found that three of the four hallmarks applied on French silver manufactured prior to 1789 were actually applied to the roughed-out silver sheet before the object was completed. The finished object would therefore have been subjected to multiple annealing steps during its manufacture thereby relieving the metal of any remnant deformation from the hallmarking procedure (Bimbenet-Privat and de Fontaines, 1995). This is in comparison to the English system of applying the hallmarks only after the object had been completed or nearly completed, thus the residual plastic deformation in the metal would be expected to be retained. An exception to this procedure will be discussed later.

To confirm the historical accounts of the French hallmarking procedures a sterling silver coupon was stamped with several hallmarks as described earlier. Again, the marks were polished off and images of these hallmarks were produced with the acoustic imaging technique.

The coupon was then annealed in an oven at 700° C for twelve minutes and then subjected to the imaging procedure. After only one annealing the remnant deformation has been 'relaxed' and the hallmarks can no longer be imaged (Fig. 10). Regrettably, this means that the acoustic imaging technique will not work on pre-1789 French silver objects (after this date the French hallmarking procedures were changed).



Figure 10. Effects of annealing on sterling silver. (a) A recovered acoustic image of polished-off hallmarks on a sterling silver coupon before annealing. (b) The same area after annealing the coupon.

By chance, Fig. 9 also shows additional information recovered by acoustic imaging concerning the quality of the solder join of the handle to the blade. The light colored spots inside the attachment area represent gaps/flaws in the solder join. These areas have a different acoustic response than the surrounding well-soldered metal so they are readily visible.

Another interesting chance image was obtained from a 16th century paten cover (not illustrated) during the course of imaging the hallmarks. In this case, flaws or bubbles in the cellulose nitrate coating that were not visually apparent but were quite obvious in the acoustic image.

5.4 Sterling Silver Desert Fork

Fig. 11(b) is an acoustic image of a purposely-removed hallmark from an English desert fork by Thomas Barker dating from 1808. At some period during the spoon's lifetime an owner decided to add the monogram "M" to the back of the handle. In order to accommodate this addition the lion hallmark was removed. Traditionally, there have been four ways of removing hallmarks and engravings. If the marks were shallow they could simply be polished away. Deeper marks could be hammered out with a subsequent thinning of the metal. They could also be filled with silver solder and finished to seamlessly blend with the surrounding metal. Finally, they could be filled by a process know as 'stoning'. In this case the surface of the silver is literally rubbed with a stone, pushing the surrounding metal into the indentations of the hallmarks or engravings. Marks removed by hammering and stoning cannot be recovered by acoustic methods but marks erased by polishing and filling should be recoverable. In the case of the lion hallmark, its recovery probably meant that the hallmark was simply polished away. Note that in Fig. 11(a) the hallmark is very difficult to decipher; at best it can only be recognized that it is present where none was visible on the fork. The interpretation of the mark representing a lion was based on a much clearer computer image at the time the work was done.



Figure 11. Silver fork with a hallmark deliberately removed. (a) Photograph of the visible hallmarks on the fork. (b) An acoustic image of the hallmarks showing that a fifth mark was present at one time. The now missing hallmark has been interpreted as a lion.(Private collection)

5.5 Gold Coupons

The physical properties of gold suggest that it should also be a good candidate for acoustic imaging techniques. The residual stress annealing temperature for various alloys of gold varies from 173° C for 14K to 261° C for 24K and its degree of anisotrophy is nearly identical to silver. Together, these characteristics indicate that gold should behave in a similar manner as silver during acoustic imaging. To test this theory two gold coupons, one 22K and the other 18K, of the same dimensions as the silver coupons, were hallmarked and the marks polished off as described earlier.

The 22K coupon (91.66% gold) was placed in the FC-40 coupling fluid and insonified with the 20 MHz pulsed signal through an F/1 lens. A converted surface wave was captured but surprisingly, no images of the polished-off hallmarks were recovered. The experiment was repeated with the 18K coupon (75.0% gold) with only a barely perceptible image of the hallmarks recovered (Fig. 12).



Figure 12. Surface wave acoustic images of gold coupons. (a) 18K gold coupon shows just a hint of residual deformation; (b) 22K gold coupon shows no residual deformation from the hallmarks.

The explanation for these results can be found in one of the physical properties of gold, its malleability. High purity gold is extremely malleable and does not produce plastic flow when struck during the hallmarking process. Instead, the metal simply pushes aside and wells-up around the hallmark leaving no subsurface deformation to image. It is proposed that a lower purity of gold, such as 14K (58.3% gold) will exhibit some plastic deformation due to the copper content, making it possible to recover the hallmarks using the acoustic imaging technique.

6. Discussion

A total of twenty-nine silver and gold objects from widely varying time periods have been subjected to the acoustic imaging techniques. Objects imaged included spoons, forks, knives, coins, a paten cover, a trivet, and coupon blanks. Results from the modern sterling silver blanks have been very encouraging. The hallmarks were placed on the blanks in the early summer of 1997 by an experienced silversmith. These hallmarks were well and truly struck, i.e. their original existence is well documented. After the hallmarks were removed by polishing, ultrasonic imaging produced clearly decipherable images of the remnant deformation on the surface of the silver. Both surface wave imaging and back-wall imaging were clearly effective at displaying residual deformation in the silver. Where only part of the hallmark was removed, the imaging methods are able to show remnant deformation extending out from the remnant surface dents in the surface. The blanks are now approaching five years in age. Repeat images show results in 2002 that reproduce the results shown in the initial 1997 images. However, despite the clear anisotropy in silver, backscatter imaging of the silver microstructure has not yet proven effective. Neither the silver microstructure itself nor deformation of that microstructure has been shown by backscatter imaging at the 20 MHz or 50 MHz frequencies used to date. The failure of the backscatter imaging is confusing since both the back-surface reflection images and the surface wave images clearly indicate that the acoustic properties of the silver showed significant changes at the hallmark locations. The small size of the silver grains may be one factor in the inability to produce backscatter images. More work clearly needs to be done to fully understand this.

Work to recover partially obliterated hallmarks on antique silver objects has been less encouraging than the work on the coupons. But in these cases one cannot be certain that the hallmarks were properly struck in their original condition. The silver blade of the French fish knife (Fig. 9) demonstrates this case in point. The fish knife is ideally configured for back-wall imaging and yet no remnant deformation could be shown to extend from the dented marks remaining on the blade. Several different scenarios could account for this. First of all, the hallmark could have been improperly struck so that the entire mark was never there in the first place. It is also possible that the heat from the soldering attachment of the handle annealed the silver thus removing the residual deformation of the hallmark. Use and/or polishing may have partially removed the residual subsurface deformation or repeated washing in boiling water over an extended period of years partially annealed the silver. This last possibility is most unlikely as the theoretical stress

annealing temperature of sterling silver is well above the boiling point of water.

One other scenario based on the hallmarking procedure itself may also be possible. When a hallmark is applied to a thin piece of silver a 'witness mark' may appear on the reverse side of the silver from where the mark was struck. This witness mark is a raised area with the same shape as the hallmark. If this mark is visible the silversmith may wish to remove it; this procedure is called 'setting back the hallmark'. The silversmith may simply hammer the witness marks flat or can apply localized heat to that area first to make the hammering process easier and less likely to cause any damage to the surrounding metal. In the case of flatware, the hallmarks were frequently applied to the back of the handles before they had been wrought to their final shape. This allowed the assay office to place their marks completely on the silver and still allow the metalsmith the freedom to produce a slender handle that in the final shape would not provide sufficient space for the hallmarks; the final shaping would have certainly involved heating the metal. This local annealing effect would then diminish the ability to produce an image of the hallmark using acoustic methods.

Surface wave images of two antique coins (not illustrated) suggest that downward or compressive deformation (i.e., a dent) is more readily defined than the upwelling of material. Efforts to image the originally upraised patterns of the years in which coins were struck have not yet been successful. This suggests that the deformation under dents is more readily detected than bulges. Also, since both sides of a coin are struck at the same time there will be some mixing of subsurface deformations making it more difficult to separate individual elements of the design (e.g., the date).

7. Conclusion

The success rate for acoustic imaging of worn-off hallmarks on the twenty-nine objects in this project has been approximately ten per cent. While this initially appears to be fairly unsuccessful, the project has succeeded in producing images one hundred per cent of the time where remnant plastic deformation exists. When the deformation no longer exists either through being poorly struck, being annealed out, or completely worn/polished through the zone of deformation, acoustic methods cannot produce an image. Unfortunately, there are no visual clues on the surface of the metal that will permit speculation on the success or failure of the acoustic imaging technique. Each object will have to be imaged individually to determine if there is any residual deformation to be found.

Worn hallmarks on objects manufactured from high purity gold cannot be imaged with the acoustic methods as described here. The historical standards for objects made of gold have been 18K or greater. It is suggested that at this purity gold is too malleable to produce plastic flow when struck in the hallmarking process. As the quantity of alloying metal in gold increases (corresponding to a decrease in the purity of the gold) the chances for the acoustic recovery of

worn hallmarks and inscriptions should increase but this has not yet been proven experimentally.

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Materials

FC-40 Fluorinert Brand Electronic Liquid: a perfluoro liquid containing no hydrogen or chloride: 3M Specialty Materials, 3M Center, St. Paul, Minnesota 55144-1000 USA. (651-737-6501).

Acoustic Transducers: Panametrics, 221 Crescent St., Waltham, MA 02453 USA. (781-899-2719)

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FOUR BEAKERS OR TWO BEAKERS? ONLY YOUR CONSERVATOR KNOWS FOR SURE...

Stephen P. Koob

1. Introduction

This is an interesting story, and I should start with the title, which isn't entirely correct. In 1964, the Corning Museum of Glass was given numerous fragments of what was thought to be a glass bottle (a base section), and fragments of a beaker, identified as such because of the conical shape and simple rim. In 1967, more similar fragments were given to the Museum, again of another beaker and bottle, or, at least, this is how they were first published (Megaw 1968; Fig. 1). At various times in the past 35+ years, researchers, curators, conservators and directors have looked at the pieces and thought they were anything from four beakers, to two beakers and a bottle, to two beakers.

After the fragments were assembled in1967-1968, as best as possible, they were catalogued as four separate "Byzantine beakers, gilded and scratched-engraved". This is the way they remained, even through my first tenure at Corning, when I first looked at them at the request of the director, Dr. David Whitehouse, who is also curator of ancient and Islamic glass at the Corning Museum of Glass. At that time, I thought there wasn't much more that could be done. I left Corning in 1994, but interestingly, when I came back to Corning in 1998, the Director asked if we could look at the fragments again, together. So we did, and we reviewed the 1968 publication by Peter Megaw (Megaw 1968), which states clearly that the two center sections have similar decoration, and the other (outer) two sections are similar to each other, and differ from the center sections only "in that the roundel borders are formed by three concentric lines" (Megaw 1968, 101; see Fig. 2). On the center two sections, the roundels are surrounded by 4 concentric lines, with dots in the middle (Fig. 3). This led to the question that we then discussed, "could two and two possibly go together?". Regardless as to the answer to that question, Dr. Whitehouse wanted me to "improve their appearance" and find some way to mount them, because he wanted to re-publish them. Putting two and two together sparked my interest, and after many trips to the microscope, I finally thought I could prove that there were just two beakers.

2. The Beakers

The beakers truly were magnificent, and it's sad that we only have fragments and just a hint at the original decoration. They are made of transparent dark blue glass, the dark blue confirmed as cobalt, as analyzed by Dr. Robert Brill (Brill 1999), the research scientist at the Corning Museum of Glass. The fragments vary in thickness from 0.5 mm - 1.2 mm, and also vary in appearance because of that. The thinner areas are a much lighter blue, and the thicker areas, like the base and

rim, are almost black. Cobalt is an interesting colorant for glass, as it takes only minute amounts to impart the rich blue color that we are familiar with. Cobalt oxide (CoO), when added to a hot glass batch, goes into solution as individual cobalt ions within the glass. The resulting blue color, even when dark, is virtually transparent in transmitted light, and is very difficult to match with modern pigments or dyes. The modern cobalt pigment is a compound of cobalt and aluminum hydrate (CoO \cdot Al₂O₃). This pigment only disperses in solution, thus giving a very different color, owing to light reflection. This was going to give me problems later on.

Both of the beakers were blown, as evident from the shape, and were also scratch-engraved, gilded (Fig. 4) and enameled (Fig. 5). The primary decoration consists of rows of medallions or "roundels" (Fig. 6), each of which contains a bird, but in three different postures, one facing left, one facing right (see Fig. 2), and the third bird, facing right, but with its head turned back (see Figs. 4 and 6). In close-up, it can clearly be seen that all the birds, the floral "filler" decoration, the dots, and framing borders all had gilding, applied as paste and not gold leaf. Even the fragments that appear visually to have no decoration left, under the microscope, can be seen to have traces of gilding present. The enamel, either yellow, or yellow and white, was used for the outer concentric line around the roundels.

Dr. Whitehouse now dates the pieces to the end of the 12th early 13th century (Whitehouse 2002), and the fragments may have come from a Byzantine castle in Paphos, Cyprus. There are comparable pieces from other sites around Paphos (Megaw 1959). Where they were actually made is unknown, but most likely Rhodes or Western Anatolia.

3. The Conservator as Detective

This leads me to one of my most important recommendations for the restoration of glass, which is to use a good binocular microscope. A microscope is useful not only for the joining of fragments, but also to see decorative elements as well as techniques and details of manufacture. It was through the use of the microscope that I determined two of these sections belonged together. Obviously the fragments and sections look similar, so much so that one would suggest that they were made and/or decorated by the same person. But let me review some of the indicative factors that can help us join fragments together. These are specifically for glass, but can also be transferred to other materials: shape, size, color, thickness, light transmittance (or not), curvature, decoration, surface wear or weathering. Blown glass also has air bubbles, which are often directional. Finally, for transparent glass, there are compositional anomalies, such as inclusions or seeds and the non-homogeneous mixing that one gets with colored glasses (Fig. 7). This is particularly true of early glasses, where the initial glass was most likely a clear batch, and a darker colored glass was ground up and mixed in to give the desired color. The darker glass rarely mixes in perfectly, and one sees streaking of the darker color, not unlike what you would see in a marble cake. This can be seen, using a microscope and transmitted light (Fig. 8).

Through the microscope it was fairly easy to see that two of the sections belonged together, even if the joining surface was not very convincing. Under magnification and transmitted light, it can be seen that the air bubbles match, and line up vertically from one broken fragment to the next. In addition, the streaking line of minute bubbles and lines of darker blue color continue across one fragment and in to the next (Fig. 9). The surface decoration (in reflected, incident light) lines up as well, and supports the microscopic findings.

In the end, I was convinced. I showed my discovery to Dr. Whitehouse, and he was also convinced. In fact, he wanted me to devise a way to display it. Well, I thought about mounting the two sections, one on top of the other, and then decided I would at least start by redoing the restorations.

4. Re-assembly/Re-treatment

The fragments really needed a better restoration, since the previous repairs were not perfect, and after 35 years the few fills had discolored and become loose. At some point tape had been added to hold the fragments together. The fragments were taken apart, cleaned and reassembled using B-72 adhesive. B-72 really works very well with glass (Koob 1986; Koob 2000), but again, a binocular microscope is very helpful. Under magnification, joins can be lined up absolutely precisely. For glass repair, I recommend that the B-72 adhesive is a little thinner than my original published recipe (Koob 1986), which can simply be done by evaporating off less solvent during the adhesive preparation, for example, evaporating off 40-42g of acetone from the original 100g (Koob 1996).

5. Loss Compensation

Losses were then filled using plaster of Paris, with the long range plan of later using the plaster fills to make detachable epoxy fills. This is a technique that I gave a paper on at the IIC Congress in Melbourne (Koob 2000). The plaster fills were easily detachable, since plaster does not bond well to glass. The plaster was then sealed with shellac in anticipation of later casting and molding. I felt the shellac would give a better surface, more approximate to the glass than B-72. The top and bottom sections were then joined together using plaster fills, and the "two" beakers were now one (Fig. 10).

Just about the time I finished this, Dr. Whitehouse came back and said, "Well, what about beaker number two?". He now added that not only did he want to republish them, but he wanted to put them up on display in our "Recent Acquisitions Case", because, in his mind they were now two new acquisitions, and not four fragmentary research fragments. That was in January of 2001, and again I thought of just mounting those two sections, because so much more is missing, with only approximately 35-40% of the whole preserved. I began by making a large tubular section of

plaster and was thinking of mounting the fragments onto that, but it just was not a good idea. The plaster was much too heavy and it would have taken so much difficult chiseling and cutting. So, instead, I took the two sections apart and started reconstructing them. When I got both the top and the bottom sections completed, and fills done to the top of the preserved glass, I took another look at the completed beaker (# 1), to see the pattern and order of the roundel decoration (Fig. 11). The birds in the top and bottom rows are in the order Right-Left-Back, and in the middle row are offset, Left-Back-Right.

Comparing beaker # 1 to beaker # 2, the sequence for the top and the bottom rows of roundels is identical, and it seems likely that the center row would have been the same as well. There is only one small bit of a bird preserved in the middle section, and that is a foot that joins to the bottom section. But enough of the roundel is preserved to show that the bird had to be facing left, which confirmed that the order of the birds was the same on both beakers. The final assembly was done similarly to the first beaker, using a paper cup as an interior backing (Fig. 12) and to keep the sections in the right position. Plaster was then applied to connect the two sections (see Fig. 12), and was then trimmed and finished. One side was done at a time, and it was even possible to float in some fragments (Fig. 13), because I knew exactly where they went, since the bird decoration is so distinct. Reconstructing a vessel that is missing 60% is quite a challenge (and a lot of plasterwork) but it does present the fragments in an understandable and stable order.

The second reconstruction took less than 2 weeks, whereas the first one took probably close to 10 times that. The main mistake I made in the first reconstruction was working solely from the bottom up, and in this case, it just didn't work, because I really did not have a good idea of the center diameter, which is actually the main reason the sections were originally thought to all be different vessels. The diameter of the upper part of the beakers is dramatically larger than the bottoms, or even lower sections.

The beakers needed to go on display, so I painted the plaster a dark cobalt blue, which looked fine with incident light, but looked very purple in color photographs, especially in close-ups and under strong raking light (Fig. 14). Mounts were made for both beakers, and they went on display for 6 months.

6. Detachable Epoxy Fills

In November 2000, the beakers came off display and I had the chance to start redoing the fills in tinted epoxy. This was easier said than done, because I have been trying for years to get a good match for cobalt blue in glass, and had been generally unsuccessful. However, my last intern offered to bring me back some dyes that she had experimented with in France, and I did find one that worked perfectly (Macrolex Blue RR, by Bayer), with a little help from some red and black dyes (Fig. 15).

Briefly, the procedure is to take molds of the plaster fills, and then cast tinted epoxy into the molds (Fig. 16). I used Epotek 301 for all of the castings, primarily because of its faster setting time. I have found that single enveloping molds work the best for this, rather than trying to cast two-sided molds. As long as the silicone rubber is thick, you can cut it, remove the plaster

fragment, and it retains its shape for the epoxy casting. The resulting "epoxy fragment" is only going to be as good as your plaster fill, because silicone rubber is very unforgiving, and it will copy every minute detail, scratch or flaw, and uneven surface. In addition, it's virtually impossible to imitate smooth glass, much less smooth glass that also has the remnants of scratched, enameled and gilded designs.

So, I took the first beaker completely apart; which was easily accomplished thanks to the B-72 adhesive. All the blue overpaint was cleaned off and since I was disappointed with both B-72 and shellac as a coating, I decided to try Krylon spray, which worked extremely well. Still, there was quite a bit of unevenness from the differing thickness of my plaster fills, and from scratches and imperfections that I hadn't sanded or worked out. I made up a big batch of colored resin (it helps to mix the dyes in at least 24 hours in advance anyway), and kept it in the refrigerator. The final results matched the original glass fragments very closely. A layout of original fragments with fills in reflected light (Fig. 17), and the same group in transmitted light. (Fig. 18) shows how successfully the casting and molding turned out.

7. Final Assembly

The fragments and epoxy fills were then assembled using B-72 adhesive, and the completed beaker is transparent (Fig. 19), without the unnatural appearance of opaque plaster fills. Only the first beaker has been completed, and stands in contrast to the second beaker that still has plaster fills (Fig. 20).

8. Conclusions

During the reconstructions, two new joins were found, one on each beaker; and only three fragments were not used. One fragment, incorrectly positioned on beaker # 2, now joins beaker #1, and one fragment not originally joined to beaker # 2 was joined. As noted above, beaker #1 is finished, and it is difficult to decide whether to redo all of the fills on beaker # 2, or just the areas in contact with the glass. The next tricky job will be to light the pieces on display effectively, and to show off the transparency of the glass as well as the decoration.

Finally, I'd like to say that this is not an easy process, but the results really can be spectacular. I molded all the plaster fills and cast the epoxy fragments all at once, and that took about two weeks. There was a little bit of touch-up and reworking of the epoxy fills after casting, but even with that, the final reassembly took less than two weeks.

Acknowledgments

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Materials and Suppliers

Acryloid B-72, Conservation Resources, International, LLC, 8000-H Forbes Place, Springfield, VA 22151, Tel. 703-321-7730.

Epotek 301, Epoxy Technology, 14 Fortune Drive, Billerica, MA 01821, Tel. 1-800-227-2201.

French's "Diamond 'P'" dental plaster, Samuel H. French, Co., 4446-50 Cresson Street, Philadelphia, PA, 19127, tel. 215-482-6770.

GI-311 Silicone Rubber, Plastic Tooling Supply Co., 303 Commerce Drive, Exton, PA, 19341, tel. 610-363-5440.

Macrolex Blue RR (dye), Bayer, Geschäftsverelch Farben, Marketing 3.3, 5090 Leverkusen, Germany.

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Figure 1. Fragmentary sections of "four" beakers, as catalogued in 1967.



Figure 3. Detail of roundel with four concentric lines, with dots between the middle two lines.

Figure 2. Detail of roundel, showing three concentric lines.



Figure 5. Detail of roundel with enamel (lightest areas).



Figure 6 - Almost complete roundel, with bird.





Figure 8. Streaking of cobalt color across two broken fragments, with transparent fills in between.



Figure 10. Reconstructed beaker # 1, with plaster fills.

Figure 9. Partially restored section showing vertical air bubbles and streaks of cobalt across glass fragments. Areas with no bubbles are fills.



Figure 11 - Drawing showing pattern and "order" of roundels and birds.



Figure 12 - Applying plaster over paper cup "backing" to join the two sections together.



Figure 14. Detail of beaker after painting. Under strong light the cobalt blue paint appears purple (much lighter).



Figure 15 - Mixing blue dyes in epoxy: tests and castings.



Figure 16 - Casting of tinted epoxy into silicone rubber molds.



Figure 17 - Rim fragments and tinted epoxy fills in reflected light (beaker #1).



Figure 18 - Rim fragments and tinted epoxy fills in transmitted light (beaker #1).



Figure 20. Two beakers with mounts. Beaker # 1 on the left, has transparent blue epoxy fills; Beaker # 2 on the right has painted plaster fills.

MINA'I WARES: DISCOVERY OF A 13th CENTURY ISLAMIC CERAMIC TRANSFER TECHNOLOGY

John Hirx

Mina'i polychrome ceramics were made during the 13th century in Iran. They are characterized by their almost white body; most probably of fritware composition. Glazed most often with an opaque white glaze, the wares are sometimes glazed with other colors such as turquoise or even purple. They are most noted and identifiable by their very unusual overglaze polychrome enamel painted decoration (Lane 1947; Grube 1976).

Bowls, decorated both internally and externally, beaker and bottle forms, and even some pressmolded tiles, are typical mina'i object types. The bowls, which vary in shape and size, tend to account for the greatest population of wares within the production. Overglaze enamels were used to create images of humans, animals, arabesques, calligraphy, etc. on the surface of the glazed wares.

Historically, the imagery that decorate mina'i wares has been thought to be enamels painted onto the glazed surface. Microscopic examination of many of these pieces reveals that the imagery may have been made by means of a transfer technology in which enamel paint was used to create images independently from the ceramic form. The painted images were then transferred to and fired on the glaze surface, fusing the enamel in place.

Ceramic transfer technology has been historically attributed to the English who have been credited with inventing this technology in the 18th century (Drakard 1995; Wymna 1980; Coutts 2001). However, a survey of mina'i wares in various national and international collections strongly demonstrates that mina'i enamel decoration may be the earliest known example of ceramic transfer technology.

A fine example of mina'i ware that can be used to illustrate and develop a working theoretical model of the earliest example of ceramic transfer technology is a ewer in the collection of the Los Angeles County Museum of Art (Figs. 1 and 2).

The raw materials from which this and other mina'i forms are made is probably fritware. A fritware body is fairly consistent. It is composed of one part sticky white clay, one part frit and ten parts white sand. Frit is a type of ground glass specifically prepared to act as a material with a low melting point to consolidate and initiate fusion of the component of the fritware, i.e., the sand and clay. The base glaze is most often a white, tin opacified lead alkaline glaze, that may utilize the same frit found in the body as its primary ingredient to promote proper adhesion between glaze and body (Allan 1973).

Photomicrographs of a fritware body in cross-section (Figs. 3 and 4) are useful for studying the

relationship between clay body, glaze, and overglaze, as well as understanding what the body is made from. Fig. 3 shows three layers; the ceramic body, glaze, and overglaze enamel. In Fig. 4, the individual quartz particles that account for the majority of the ceramic body are angular white to gray grains.

Until recently, the overglaze enamel decoration of the mina'i wares was thought to have been painted in a very straightforward manner, which is to say that the vessels were thrown or press molded, bisque fired, glazed and glost fired. After this, overglaze enamel paint and gilding were applied directly to the glaze and fired again. If the casual viewer were to see an example of mina'i on display, they would probably notice characteristic "crazing", which is the formation of countless cracks in the glaze.

Crazing is a glaze fault, incurred when the clay body and glaze do not "fit" to each other correctly. The glaze is too small or under tension in relationship to itself and the clay body. At room temperature, the glaze is attempting to shrink, resulting in the formation of some cracks. When the clay body and glaze respond to fluctuations in temperature, expanding and contracting, the clay body expands more than the glaze, causing it to craze, releasing stress in the glaze layer.

Craze lines are very easy to distinguish in the white glaze because over time, the cracks fill with grime and dirt and discolor to a warm gray-yellow coloration. It would seem plausible that because the glaze crazes, the enamel layer above the glaze crazes on the same lines.

When casually examining mina'i wares, what appears to the naked eye as crazing is found on close inspection to be independent movement of the design. The enamel has not crazed, nor is it related to any crazing that exists in the base glaze. The apparent 'crazing' in the enamel of mina'i wares is not accompanied by cracks formed during cooling to relieve post-fire tension. Curators have suggested that the movement in the enamel my be attributable to a runny glaze.

The closest parallel is in transferware technology. Transfers, in ceramic terminology, are more commonly called 'decals'. The modern ceramic decal is the descendent of historic transfer technology. Everyone has seen and lives with ceramic decals, which can be found on any coffee mug bearing the insignia of a favorite sports team or logo (Fig. 5). Transfers are independent images created from ceramic raw materials, i.e. enamels. After creating the image, it is applied to the ceramic for a final firing.

The English have been traditionally credited with "inventing" the decal in the mid 18th century. The plate in Figure 6 is an example of an early decal decorated ceramic. On of the earliest people to employ this technique was John Sadler of Liverpool in 1749. John Sadler and Guy Green of Liverpool, applied in 1756 for the patent for the glue bat method (Figs. 7 and 8). Transfer technology, in the case of English ceramics, allowed a complex image which could not be painted directly on the surface of the object to be created independently and then applied to the ceramic (Drakard 1995).

"Bat printing" was the first transfer system employed. In this system, images on old out-of-use copper etching plates, which had been engraved or etched to create an image for such things as newspapers, were "inked" with linseed oil. The plates were then coated with a ¹/₄" thick layer of animal glue to form a "glue bat", which when cooled, was peeled from the copper etching plate, picking up the oil from the plate. The bat in turn was pressed onto the ceramic to transfer the oil (Fig. 9). The oil image on the ceramic was then dusted with pigment and fired (Fig. 10).

The glue bat method was shortly supplanted by the tissue method (Fig. 11). Patents for this technology were applied for both by John Brooks (a Birmingham engraver) between 1751 and 1754, and Harry Baker in 1781. In this procedure, paper coated with gum arabic was applied to the plate and pushed through a press to "capture" cobalt containing ceramic "ink" which had been applied to image-bearing copper plates. The sheet of tissue was then pulled from the copper plate and transferred to the ceramic surface and fired. The tissue burned off during the firing, transferring the image onto the glaze.

There are advantages and disadvantages to both methods. The disadvantage to the glue method is that the bat flexes too much, both expanding and contracting the image that is being applied. It also is easy to smudge the transferred oil or dusted image. Its advantage is that it fits concave and convex contours well.

The advantages and disadvantages of the tissue method is the reverse of the bat method. In the tissue method, if the tissue tears, which it often does, both unintentionally and intentionally, a diagnostic transfer fault is incurred.

In fitting the tissue, i.e., the support, it is difficult to disguise where the tissue overlaps. Attempts to disguise the overlaps often result in tears, losses, shifted images, etc. Various cuts and disruptions can be seen in the application of the tissue image to this late 19th century, early 20th century porcelain (Figs. 12 and 13).

Today, the most widely used mass-production method of applying an image is by paper transfers or prints from lithographic plates. Instead of substituting oil for normal printer's ink, varnish is used to ink the plate, then transfer paper is pressed onto the surface to pull varnish from the plate. The varnish is then "inked" and the tissue paper transferred to the ceramic. The other printing option is to have the glue bat attached to a flexible piston that off-set presses onto a plate, pulls the varnish, then presses it onto a ceramic surface where it is dusted with ink.

Decals can also be made by silkscreening an oil-based ceramic material onto a gum-based paper. The decal and film are transferred to a ceramic, pressed in place, and fired during which time the support burns off (Fig. 14).

The ceramic faults associated with transfer technology previously discussed, that is, the disruption of the carrier of the enamel paint causing such things as tears and shifted images, can be found on mina'i wares.

When examining mina'i in museum collections, three scenarios are usually encountered.

1. Microscopic examination clearly shows the ceramic faults associated with transfer support movement. The faults include: broken individual painted lines, arabesques that split and move sideways (Fig. 15) or spin, splices through the support which were carefully laid down but detectable through the microscope, large areas of multiple layers of color that break cleanly and move apart (Figure 16), splits that move through numerous areas of unattached, independent color, and tenting of the enamel support.

2. Microscopic examination shows that vessels are heavily overpainted so that distinguishing the ceramic fault is impossible without removing the overpaint. These vessels cannot be fully studied at the time.

3. No ceramic faults can be found, which identifies the mina'i as either directly painted or simply a well done, fault free transfer. This is the case with the Freer beaker, perhaps the most famous example of mina'i ware (Freer Gallery of Art, Smithsonian Institution, # 28.2).

In order to prove and substantiate the working hypothesis that mina'i is the earliest example of transfer technology and that it was developed earlier than previously thought, colleagues JoAnna Rowntree, Amy Green and I have begun to experiment and explore replicating the mina'i technology in order to duplicate the technique of using overglaze paint on goldbeater's skin. We have bought a variety of overglaze enamels and have stretched the goldbeaters' skin over an image in order to copy and transfer images to a low-fire ceramic. Goldbeaters' skin was chosen as the enamel support, since it would have been available in the 12th century and could exhibit faults. This is still an experiment in process. We have yet to replicate the exact procedure.

One might ask: Why create a design in this manner? It is true that the Islamic world had many wonderful, gifted painters. However, the paintings that have survived from this period are primarily wall paintings. Wall paintings and miniature paintings are flat; vessels are not. Mina'i wares vary greatly in size and shape as well, which demands a flexible painting technology.

Painting and constructing an image on a flat surface is quite different from creating a composition on a convex, concave or three-dimensional surface. One approach to construct images on non-flat surfaces might employ the use of grids. Grids could have been drawn on vessels prior to the application of paint and gilding to aid the painter in order to orient and proportion their composition. Known examples of fitting a design to a convex, round ceramic can be found in contemporary American Indian ceramics, such as Acoma pottery in which the artist first drew on the vessel to make the design fit, making adjustments along the way.

Mina'i painting varies in both in quality and compositions. The finest example examined to date is a fragment that shows a portion of a head in the collection of the Metropolitan Museum of Art. In the creation of mina'i ware, no matter the level of quality, someone was spending a great deal of time trying to compose a series of images, whether figural, floral, or geometric for a surface on

which everything had to fit properly. The upholstery of numerous images on a convex or concave surface is challenging. Goldbeaters' skin, which may have served as the support for the painting, allowed the painter to position and reposition his images to fit the surface and composition at will, simply by keeping the surface moistened with water. Further examination is needed to determine the exact process.

Modern decals are of industrial interest since the same image can be created repeatedly for mass production purposes. The Islamic decal, I believe was not being created with this purpose in mind. The decorator had discovered a way, I believe, by which a complex composition could be created without disturbing individual components of the composition.

This project is still very much a work-in-progress. After examining wares in the collections of the Miho Museum, Los Angeles County Museum of Art, the Walters Art Gallery, The Metropolitan Museum of Art, the Freer/Sackler Galleries and the Victoria and Albert Museum, I am convinced that we are not looking at a runny glaze.

It has become consistently clear that the enamel was painted onto a support that shrank and moved in a variety of directions. The transfer theory, or a variation thereof, may still work. However, there are still many steps that need to be clarified in order to resolutely state that transfer technology was strictly the technique that was being used on these wares. If this is proven, then the credit for this invention belongs to the Islamic world, preceding the English patents by 500 years.

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Figure 1. Mina'i ceramic ewer. Los Angeles County Museum of Art, M.2002.1.7, The Madina Collection of Islamic Art, gift of Chamilla Chandler Frost. Late 12th-early13th c., Iran.



Figure 3. Cross section of fritware fragment



Figure 4. Magnified quartz grains in the fritware



Figure 5. Modern ceramic mugs with decals



Figure 6. English porcelain plate, 18th century, with decals (Los Angeles County Museum of Art, 50.28.17).


Figure 7. Application of oil to copper plate (from Scott 1994).



Figure 8. Application of "glue bat" to the oil laden copper plate (from Scott 1994).



Figure 9. Transfer of oil image on the glue bat to the glazed ceramic (from Scott 1994).



Figure 10. Dusting the oil image with ceramic pigment (from Scott 1994).



Figure 11. Lifting a tissue transfer from an inked copper plate (from Scott 1994).

Hirx



Figure 12. Late 19th century blue-on-white porcelain vase with transfer image (collection of the author).



Figure 13. Splice through the transfer design on the vase in Figure 12 at high magnification showing hidden upholstery of the decal to the glaze surface.



Figure 14. Application of a gum based paper design onto a pitcher (from Chandler 1968).



Figure 15. View of transfer image from LACMA ewer M.2002.1.7 showing split decal.



Figure 16. Enlarged microscopic view of Figure 15.

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A TECHNOLOGICAL STUDY OF THE PAINTED SURFACES OF ZAPOTEC URNS FROM XOXOCOTLÁN

Samantha Alderson

1. Introduction and Background

Figural ceramic urns are among the most recognizable and important artifacts of Zapotec culture, a civilization that flourished in Oaxaca, Mexico from approximately 900 BC until AD 900. Hundreds of Zapotec urns are in museum collections around the world and they have been published widely. However, beyond authentication studies, little technological information about these important artifacts has appeared in the literature. In 1994 I had the opportunity to begin a technological study of Zapotec urns in the collection of the American Museum of Natural History, with funding from the Kress Foundation. The study has included investigation of construction techniques and ceramic analysis but has focused primarily on examination of the painted surfaces of the urns, and it is this aspect of the research that will be presented below.

Past studies of Zapotec urns have focused on iconography. Scholars have traditionally described and categorized the urns as deities - representations of members of a Zapotec pantheon of Gods (Caso and Bernal 1952; Boos 1966). It has more recently been suggested that they were connected to the practice of ancestor veneration, which was an integral part of the Zapotec religion (Marcus 1983; Marcus and Flannery 1996). They are generally found in association with tombs, but there remain many unanswered questions regarding the function of the urns within the burials. They appear to be constructed as vessels, but are almost always found empty. It has been suggested that they may have held an organic substance, possibly a liquid, which has decomposed or evaporated over time, but to my knowledge, no residual analysis has been done on freshly excavated urns to test this theory. It has also been suggested that the vessels were intended to hold "spirit" or other non-corporal force (Boos 1966; Marcus and Flannery 1996).

Each urn is a cylindrical vessel open at the top and fronted by an anthropomorphic or zoomorphic figure frequently obscuring the vessel behind it. The figure is most often seated cross-legged with hands on knees and wears an elaborate headdress. There are numerous variations in position and attire. They can vary greatly in size. Many are less than a foot high, while others are life-sized, or larger (Figs. 1-3).

These low-fire ceramics can be quite complex constructions, assembled before firing from numerous components. Some were made using only hand modeling and carving techniques, while others include press-molded elements. Past studies have usually reproduced the urns using black and white photographs or drawings and surface decoration has often not been addressed. Based on personal examination of Zapotec urns in museums in Mexico and the United States and extensive review of the literature, it appears that almost all urns have traces of post-fire paint. A few examples have full polychromy, but most do not appear to have been elaborately painted. The

absence of complex paint schemes is probably partially responsible for the historic lack of interest in the surface decoration of the urns. This has no doubt been compounded by the fact that the paint on Zapotec urns is usually very powdery and friable, and thus often badly preserved.

The collection at the American Museum of Natural History contains approximately 80 urns and more than 100 urn fragments. This is to the best of my knowledge the largest collection of Zapotec Urns outside Mexico. Several of the urns and fragments in the Museum's collection have remarkably intact painted surfaces making them particularly good candidates for pigment study. These well preserved pieces belong to a part of the collection that was excavated by Marshall Saville, the museum's first curator of Central and South American archeology, in the late 1800's and early 1900's.

The Saville collection presented a unique opportunity to conduct a technological study of a significant number of urns that were known to be authentic. The unquestionable provenance of these urns was crucial since only a small number of the thousands of known urns have a documented archaeological context and apparently there are a great number of forgeries, many with very early collection dates. Several published thermoluminesence studies have exposed numerous fakes in collections around the world, and it is now often assumed that urns are suspect unless proven otherwise by documentation or analysis (Mongne 1987; Shaplin 1978).

Most of the Saville material was excavated in 1898, at the site of Los Mogotes de Xoxocotlán (Saville 1989 and 1904). The site is located in a valley less then 5 km from the Zapotec capital of Monte Albán, which at its height in the 6th and 7th centuries AD had a population of approximately 24,000 (Marcus and Flannery 1996). It has been suggested Xoxocotlán may have served as an agricultural center or marketplace for this capital city (Kowaleski 1983). There are 12 urns and 30 urn fragments from Xoxocotlán in the museum's collection, and all appear to date from the classic period of the Zapotec culture, roughly from AD 200 – 700.

2. Surface Examination

The surfaces of the Xoxocotlán urns were carefully examined using a binocular microscope prior to removing pigment samples for analysis. This often revealed the presence of designs or pigments that were not apparent to the naked eye and had not been previously noted when the urns were published by Saville or cataloged into the Museum's collection.

The three large urns Saville found in Mound 9 have the best-preserved paint of all the urns found at Xoxocotlán (Figs. 4, 5). These are part of a set of five urns that were placed in a row above the doorway to Tomb 3. (The other two urns, like much of the material from Xoxocotlán remained in Mexico in accordance with an agreement made prior to the excavations.) The fronts of the urns are covered with a layer of red pigment, much of it preserved under a compact layer of burial soil. At first it appeared that red paint once covered the entire fronts of these urns. However, upon further examination it became clear that there are no significant traces of red, or any other color,

on the central medallions in the headdresses. These medallions appear to have been unpainted, while the rest of the urn fronts and much of the tomb front were also painted red. This design would have greatly altered the visual impact of the urns, accenting the glyphs, which would have stood out very strongly in the overall tableau of the façade.

Unfortunately, not all the urn surfaces are as well preserved as those from the façade of Tomb 3. In Mound 7, Saville uncovered a second set of five large urns, two of which are in the museum's collection (Figs. 6, 7). These urns were not built into the façade but placed in a row on the ground in front of Tomb 1. At first it appeared there was very little pigment on these urns but careful examination revealed small traces of red overall, often heavy in interstices or other protected areas. There is enough pigment remaining to say that most of the surface was probably once painted red but too little to determine a pattern in its application.

A smaller more elaborately painted urn was also found in Mound 7, lying on a section of ceramic tubing leading down to the tomb (Fig. 8). The urn has a finely modeled face and is ornately dressed wearing a complex headdress. Although the traces of paint are faint in many areas, it was possible to sort out some of the original decoration. The plaited headdress and teeth were painted white. There are traces of yellow pigment on the face from the nose down, while the upper half of the face and the lips are painted red - a type of bicolor face decoration that is found elsewhere in Zapotec pictorial art. The hair, ears, arms and parts of the ear ornaments are also clearly painted red. The painted surface on the lower half of the figure is severely damaged. There are clearly remains of both white and red paint, which overlap in some areas, perhaps indicating that at least parts of this urn were repainted at some time.

Evidence of repainting is also found on the small urn that Saville found in a niche above the entrance to a Tomb 2 in Mound 8 (Figs. 9, 10). In this case the painted surface is fairly well preserved, probably because like the urns from Tomb 3, it was placed in the façade of the tomb and the surface was protected to some degree during burial. Most of the front of this urn is covered with red paint. On much of the surface the red pigment is applied directly to the ceramic body, however in others areas it is clearly on top of a layer of white paint or stucco. In addition, a third layer of paint was visible under magnification in some areas, including the grooves between the toes. A cross-section of the paint from this location showed three layers of paint: red on the surface, a white underlayer, and below the white layer, a second red layer applied directly on the ceramic.

Although the order and distribution of these layers is unclear, it certainly appears that the urn was repainted on at least one occasion. This is important evidence that it may have been used in a previous burial or perhaps in a different context before it was placed in the façade of the tomb. In addition, red pigment found on the old break edges at the loincloth and headdress of this urn offers further evidence of reuse. It appears that the vessel was painted and placed in the tomb façade after these parts were lost.

3. Pigment Analysis

Once the surface examinations of these and the other urns from Xoxocotlán were complete, pigment on all the urns and urn fragments were sampled for identification. More than 100 pigment samples have been taken from urns and related material from the tombs at Xoxocotlán. The pigments were identified using microchemical tests, a polarizing light microscope, and a scanning electron microscope with energy dispersive spectroscopy.

A literature review conducted prior to sampling revealed published analysis of pigments from other areas of Mesoamerica, mostly of Maya murals (De Hanau et al. 1966; Gettens 1955; Hansen et al. 1995; Magaloni et al. 1995; Merwin 1931; Shepard 1946), and analyses of murals at Teotihuacan (Littman 1973; Torres 1972). However, there are very few analyses of Zapotec painted artifacts (Castillo 1968; Olvera 1994). For this reason it was decided to sample pigments not only from urns but also from other painted artifacts excavated at Xoxocotlán. These included human and animal bones, mural fragments and painted stucco sculpture. The broader sampling provided a more complete picture of the Zapotec palette and supplied comparative material for the analysis of the pigment samples from the urns.

The results of the pigment analysis are shown in Table 1. Red is clearly the most widely used color in the burials at Xoxocotlán. Red is also the predominant color throughout ancient Mesoamerica. Red paint is found on the earliest painted pottery in Oaxaca, and continues to appear in abundance on architecture, murals, sculpture and other objects. In burials it is found smeared on walls, thrown over objects, dusted on floors, and applied to human remains (Boone1985; Marcus and Flannery 1996; Miller 1995).

Colors	Pigments	Total	· · ·	Urn			
		Objects	Urns	Fragments	Stucco	Murals	Bones
White	Calcium Carbonate	7	3	1	1	2	0
Black	Carbon	2	0	0	0	2	0
Yellow	Geothite (Iron Oxide)	1	1	0	0	0	0
Blue	Maya Blue	1	0	0	0	1	0
Red	Hematite (Iron Oxide)	17	10	5	1	1	0
Red	Cinnabar (Mercuric Sulfide)	12	1	2	0	1	8

Table 1. Results of pigment analyses for samples taken from artifacts excavated at Xoxocotlán.

Two reds were found at Xoxocotlán: hematite (red iron oxide) and cinnabar (mercuric sulfide). Both have been previously reported on Zapotec material (Castillo 1968; Olvera 1994) and on artifacts throughout Mesoamerica. Hematite is an earthy and muted red while cinnabar is a

brighter, more intense hue. Iron oxides are very common minerals throughout the world, while cinnabar is less widely distributed. Interestingly, there appears to be a pattern in how the two red pigments are utilized at Xoxocotlán. Generally, cinnabar appears to have been used more infrequently. The red pigment on almost all the urns from Xoxocotlán was identified as hematite. Most of these objects are large and the fronts are almost completely covered with a wash of paint. This would have required a considerable amount of pigment. Cinnabar appears on a few urn fragments but only one complete urn - the smaller portrait urn found in Mound 7. This urn is not only smaller thus requiring less pigment than the larger urns, but is also remarkable for the complexity of its polychromy and the quality of the modeling. This indicates that it might have been a particularly high status object, which may account for the selection of the less common and brighter red.

Mural fragments found in Tomb 3, Mound 9, present another example of the use of the two different reds. The walls of the tomb were repainted at some time and the fragments have two distinct pictorial layers. The earlier design is partially visible in areas where the fragments are damaged. Large areas of red, blue, and white paint are visible. In this layer, where presumably large amounts of red pigment would have been required to fill in the flat areas of color, the red was identified as hematite. While in the upper design layer the red is cinnabar. Here red is used in small amounts, applied only as a wash of color on faces of the procession of figures that are drawn in black outline in the mural.

The manner in which the cinnabar is applied to the faces in this mural appears more symbolic than representational. Interestingly, cinnabar is applied in a similar manner to the facial area of a skull from the same tomb and is used exclusively on human and animal bones found in the tombs at Xoxocotlán (Table 1). Thus cinnabar is not only used more sparingly than hematite but the manner in which it is used implies this pigment may have held a distinct meaning for the Zapotec.

The other pigments found on the artifacts from Xoxocotlán are consistent with previously published analyses of paint from Zapotec and other Mesoamerican artifacts. The white samples were all calcium carbonate, black was identified as carbon, yellow as iron oxide, and the blue sample as Maya Blue. Identification of Maya Blue on the mural fragments from the tomb at Xoxocotlán is notable, since identification of this pigment for a well provenienced Zapotec artifact is not found in the literature.

Maya Blue is an unusual Mesoamerican pigment that has been widely debated and studied (José-Yacamán et al. 1995 and 1996; Kleber et al. 1967; Littman 1980 and 1982; Reyes-Valerio 1993; Shepard and Gottlieb1962; Shepard and Pollack 1971). It is now understood to be an ancient synthesized pigment, manufactured by heating a mixture of the white clay mineral palygorskite and indigo.

The blue sample taken from the Xoxocotlán mural fragments exhibits the characteristic optical and physical properties typical of Maya Blue. When examined with a polarized light microscope it appears amorphous and pleochroic with low birefringence. When tested microchemically, it

proved to be completely resistant to concentrated acids and alkalis. A sample examined with the scanning electron microscope showed the tiny rod structure typical of palygorskite (Fig. 11), and an EDS spectrum showed a composition typical of a clay mineral without the presence of elements that one would expect to find in other ancient blue mineral pigments, such as copper for azurite or sulfur and sodium for natural ultramarine (lazurite) (Fig. 12).

Maya Blue has been identified predominately on objects from the Yucatan, but many samples have been found in several other areas of Mesoamerica with occurrences spanning several eras. There is still no evidence on exactly how or where it was manufactured. It is not known if it was made by several different groups or traded over the large geographical range in which it has been found. Once more is known about the ancient manufacture and distribution of Maya Blue its presence on Zapotec material may offer evidence of trade relationships or other contact with regions outside of Oaxaca.

4. Conclusion

Even the mostly monochrome and often fragmentary painted surfaces of Zapotec urns have much to tell. Careful examination shows that the traces of pigment on the urns are often more extensive then it would first appear. All the urns and urn fragments from Xoxocotlán have pigment on their surfaces. Many urns like the ones from Tomb 2, Mound 7, at first largely appear unpainted but actually reveal extensive traces of pigment upon microscopic examination. The designs on the urns can also be more complex than one would assume. Paint was used to create detail, such as the face painting found on the portrait urn found in Mound 7, or to emphasis certain elements of the urns such as the glyphs on the urns from Mound 9. Study of the urn surfaces can offer evidence of repainting and reuse as was revealed on at least two urns found at Xoxocotlán.

Pigment analysis gives us a better understanding of the painted surfaces of the urns and the overall Zapotec palette. The identification of Maya Blue on Zapotec artifacts and the apparent selective use of red pigments at Xoxocotlán are two examples of what can be learned in this type of study.

Thus far, I have examined only a small number of urns and related material all of which are from one site in Oaxaca and so it is difficult to draw any solid conclusions. However, I believe this work clearly demonstrates that careful examinations and technological analyses hold great potential for deepening our understanding of these important artifacts of the Zapotec culture for which so many basic questions remain unanswered.

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Figure 1. A variety of Zapotec Urns in the collection of the American Museum of Natural History. Left to Right: 30/93 (H: 13"), 30/6340 (H: 6 3/4"), 30.0/1 (H: 14 1/2"), 30/6796 (8 1/4"), 30.0/2 (12 3/4").



Figure 2. Two urns from Xoxocotlan showing range of size in the museum's collection. Left: 30/6332 (H: 22") Right: 30/6340 (H: 6 3/4")



Figure 3. Side and back of Zapotec Urns from Xoxocotlan, collection of AMNH. Top: 30/6336 (H: 17 1/4"), Bottom: 30/6333 (H: 20 1/2")



Figure 4. Zapotec Urns fround in Tomb 3, Mound 9 (Xoxocotlan). Ceramic and Pigment. Left to Right: AMNH 30/6334 (H: 18 3/4 "), 30/6335 (H: 18.1/2"), 30/6336 (H: 17 1/4").



Figure 5. Front of Tomb 3 (Xoxocotlan) showing urns in situ. Photograph taken by Marshall Saville 1898. Archives of the Anthropology Department AMNH.



Figure 6. Urns from Mound 7, Tomb 1, Xoxocotlan. Left: 30/6332 (H: 22") Right: 30/6333 (H: 20 1/2")



Figure 7. Urns in situ in front of Tomb 1 (note urn on far right was removed before the photo was taken). Photograph taken by M. Saville 1898. Archives of the Anthropology Department, AMNH.



Figure 8. Urn from Mound 7 (Xoxocotlan) AMNH 30/6331 (H: 15 1/2")



Figure 9. Urn from front of Tomb 2, Mound 8 (Xoxocotlan) AMNH 30/7101 (H: 10")



Figure 10. Front of Tomb 2, Mound 8 showing urn in situ. Photograph taken by Saville 1898. Anthropology Department Archives, AMNH.



Figure 11. Scanning Electron Microscope image of Maya Blue sample from Xoxocotlan. scale = 1 micron



Figure 12. Energy Dispersive Spectroscopy (EDS) analysis of Maya Blue sample from Xoxocotlan.

A REVIEW OF ULTRA-VIOLET LIGHT AND EXAMINATION TECHNIQUES

Laramie Hickey-Friedman

1. Introduction

This presentation topic will include a brief history of ultra-violet light technology, fluorescence, and the introduction of UV examination into conservation via museums, concluding with a discussion of current research involving UV examination and possibilities for qualitative analysis. During a review of technical reports numerous notations appeared which identified restoration materials by the color of the fluorescent reflectance. Only in a handful of the reports were the materials analyzed for definitive identification. The remainder relied on visual identification. It is the author's desire to re-address this common, non-destructive technique and evaluate its usefulness and limitations in comparison to similar analytical techniques and review specifications for both qualitative and quantitative examination studies.

2. History

Fluorescence is named from the mineral fluorite, which has a faint, yet visible blue glow in response to the ultraviolet in sunlight. Possibly the earliest recorded case of fluorescence dates to the early 17th century. An alchemist, Vincenzio Cascariola, prepared a compound of phosphorescent barium sulphide (known as Bologna Phosphorus) by burning barite. An account of Cascariola's compound was published by a Professor La Galla, who had learned of the substance from Galileo (Marfunin 1979:143).

It was not until the mid 1800's that methodical scientific studies of fluorescence were undertaken. In 1810 The German romanticist Goethe noted that some minerals fluoresced. Early scientific experimenters including Sir David Brewster and Sir John Herschel identified the fluorescent phenomena as variations on known properties of light such as diffusion and dispersion (Robbins 1983: 3-13).

Repeating Goethe's work, Sir George Stokes, recognized as the discoverer of fluorescence, observed fluorite glowing from the middle of the violet region into the apparently dark space beyond (i.e. the ultraviolet band) when exposed to a spectrum created by natural sunlight. Stokes called this new physical property fluorescence after the mineral he had examined (Dake and De Ment 1941: 1-7; Radley and Grant 1954: 4-10).

2.1 Lamps

Early development of fluorescent lamps included the iron arc lamp, in 1903, which was capable of

producing abundant short-wave light (Radley and Grant 1954:11-13). That year the British Museum of Natural History created in London the first public display of fluorescent minerals, the precedent for the use of ultra-violet examination in museums.

In the 1920s and 1930s, new sources of ultra-violet light were developed. One, the argon bulb, was only able to produce low intensities. Another, known as the Nico lamp, was more effective, but very costly to manufacture. Dr. Robert Wood developed a glass filter capable of passing only ultraviolet, leading to the development of the first mercury vapor lamps. This type of lamp, known as a Wood's light, is the hand-held ultraviolet light typically found in conservation laboratories. The nickel-plated glass filter allows the emission of UV-A long wave from 320-380nm, with a peak at 365nm. Other lamps commonly used for the non-destructive examination of artwork are short wave lamps. The short wave band or UV-C runs from 180 to 280nm with a peak at 254nm.

2.2 Museums

Art historians and museum curators have long relied on differential fluorescence and the occurrence of fluorescent glues, varnishes, plasters, and plastic resins to help them detect signs of hidden repairs and forgery. The invention of the Wood's light at the end of the 1920's led to the eventual widespread use of UV in the examination of works of art. The technique was embraced by curators and later conservators for its non-destructive diagnostic capabilities.

In 1931 the Metropolitan Museum of Art published a book by James Rorimer, "Ultra-violet Rays and Their Use in the Examination of Works of Art". This is one of the earliest published examples of the widespread use of UV examination in museums. Rorimer sought to establish this technique as a valuable analytical tool for museums. It is worthwhile to note that he recommended UV photography as a means of recording the fluorescence, and for reproducibility, but made little mention of standards.

The other hallmark publication, "Fluorescence Analysis in Ultra-Violet Light", by Radley and Grant (1933), devotes an entire chapter to UV examination of museum artifacts. It cites uses of UV illumination to distinguish between genuine objects and fakes, and for the enhancement of surfaces.

3. Mechanics

To begin to understand UV examination it is useful to appreciate the mechanics of fluorescence. Simply, fluorescence is luminescence in which light of a visible color is emitted from a substance under stimulation or excitation by ultra-violet radiation. The light is given off only while the stimulation continues; in this the phenomenon differs from phosphorescence, in which light continues to be emitted after the excitation by other radiation has ceased.

The theory of molecular luminescence (fluorescence and phosphorescence) is fairly well understood. When light (or energy) hits a substance, the incoming energy will either pass through or be temporarily absorbed. This is dependent on the molecular structure of the substance and the wavelength of the energy. The energy that is absorbed by a molecule is stored as increased electron vibrational or even rotational motion, and, if there is sufficient energy, as an elevation in the molecule energy states (molecular excitation). The absorbed energy is released in the visible spectrum as the molecule relaxes. The slight shift in wavelength from the UV to the visible range is a result of prior vibrational relaxation.

Photons of visible light, and especially those of ultraviolet light wavelengths, typically have sufficient energy to cause a transition into one of the excited states. The energy must be of a type that is appropriate to the molecular structure; excitation energy that is at less ideal wavelengths may still produce fluorescence, but at a lower intensity. This explains why fluorescence occurs or is perceived differently during the examination of non-similar materials.

4. Uses

Today, ultra-violet lights are primarily used as a diagnostic tool for identifying surface inconsistencies on the object, such as inpainting or fills. UV illumination has proven to be an important non-destructive technique for initial diagnostic examination. By taking advantage of the scientific properties, surface variations can be identified and noted. Some examples of this are: sizing in paper and textiles; varnishes on paintings, and furniture; and fills and repairs on ceramics.

It is very useful during cleaning to observe the success of a treatment, or to examine a group of several similar objects looking for inconsistencies or matching qualities. The UV light is an immediate tool, easy to use, low in cost, needing only a dark room and protective glasses. Virtually anyone can see surface inconsistencies with UV light.

5. Limitations

5.1 Standards

The limitations of UV examination become immediately apparent when the technique is applied for qualitative analysis. While early scientific publications stressed the use of standards and reproducibility, this is no longer customary practice. An informal survey of conservation labs will show that there are a variety of lamps with differing emission, the UV emission is not routinely measured, and comparable standards are not utilized. While photographers tend to have a more standardized methodology, the energy sources used for UV photography tend to vary.

5.2 Detector Reliability

A recent review of 20th century conservation records and published articles yielded a number of references for material identification by visible fluorescence using UV examination. The most common of these materials is shellac, which fluoresces a strong orange color. This can become a great concern for accuracy since the detector is essentially the human eye and there can be no repeatable recording of the results.

A number of researchers from other fields, primarily petrology, have addressed procedural concerns. Of these, the classification of fluorescent color is typically foremost. It is generally agreed that a standardized system is needed, but to date a number of schemes have been used, including generalized color groups, the Pantone Color System (which is a standard in the printing industry), and the AdMark system.

5.3 Misidentification

Ambient conditions and exposure to certain rays and chemicals can have an effect on fluorescence. Previous exposure to heat may alter color and intensity, but this effect has not been studied in detail. At the outset, and increase in pressure will amplify fluorescent intensity, up to a threshold, after which the intensity will decline. Prior exposure to x-ray radiation may make non-fluorescing substances fluoresce. A similar phenomenon may occur due to exposure to some certain acids and alkalis.

In the case of resins and adhesives, there is strong evidence to suggest mixtures were often employed when restoring works of art. The shellac molecule fluoresces so strongly that in small amounts it can overpower the fluorescence of other molecules.

6. Discussion

All of the preceding information is readily available and accepted. However, what does not seem to have been addressed is whether the conservation community should look to new methods and technology to increase the knowledge gained from UV examination, and if there is a justification for improving the technique. Can conservators can improve UV examination with reproducible and qualitative results through standard examination techniques?

To answer this question it is important to examine the whole picture. Most people would still agree with James Rorimer: it is a great diagnostic tool. However, to standardize the technique we must look at the equipment and the methods employed. A variety of UV light sources are commercially available, and even lamps of the same type do not necessarily produce the same output as their filaments may emit somewhat different wavelengths. To block the visible light which is a side effect in the production of ultraviolet, manufacturers use a variety of filters which

also have dissimilar properties.

The spectra emitted by different types of lamp are even more varied. Shortwave and longwave lights produce different results in some materials. Since the shortwave light has a shorter wavelength than the long wave, the resulting fluorescence will also tend to have a shorter wavelength (Stoke's Law).

Additionally, these lamps are not very efficient when compared to the energy sources for analytical equipment. After the addition of filters, the long wavelengths are reduced to as little as 11% of the original output, while the shortwave is about 43%. In addition, both lamps and filters become more opaque over time, due to interaction of their materials with the light source (Fig. 1).

Since the brain is highly subjective with regard to color, various devices have been developed over the years to measure the intensity and color of fluorescence, such as fluorimeters, colorimeters, spectrophotometers and Raman spectroscopy. Other simpler devices may also be used, such as handheld photographic light meters. Some of these devices operate by comparing the sample to artificial light. Others use photo-cells and actually measure the wavelength of the emitted light. Another instrument to measure fluorescence is not needed. What could be useful is a way to standardize the examination of artwork with UV, a method that can be repeated and recorded.

It is not unusual for conservation to look towards other fields for adapting technology. Mineralogy, forensics, holography, and the biological sciences continue to use fluorescence. What conservation needs is a hand-held, easily portable and inexpensive method to roughly measure the visible emission of energy from the irradiated object. An analytical technique widely used in medical and forensic applications may be the answer. This is a liquid crystal tunable filter and charge-coupled device, based on visible reflectance hyperspectral imaging.

6.1 Standards

As mentioned previously, different wavelengths of excitation light may all produce some degree of fluorescence, but the intensity of fluorescence may vary significantly. Since changes in any of the fluorescent light intensities will alter the overall color, it is advisable to use the same source throughout a study.

Certain details should be recorded during examination, including the type of UV source, the distance between the source and the object, and the distance between the object and the observer (or camera). For consistency, these distances should be kept constant, and recorded. Since irradiation and other chemical alteration can influence fluorescence, it is important to know the past history of the object.

For descriptive purposes, conservators could look into adapting an existing system (such as Munsell) using the three visual descriptors of color: brightness (the fluorescent intensity),

saturation (how much white is mixed with the basic color, ranked pale, medium, deep), and hue (primary and secondary colors). In any case, exotic and potentially confusing terms (such as hazel or turquoise) should be avoided.

7. Conclusion

It is the desire of the author that this presentation promote more discussions about the use of ultra-violet examination. This technique is still a viable diagnostic tool for evaluating surface and coating inconsistencies. It is immediate, and in many institutions one of the few available, affordable techniques. With this in mind a method for recording reproducible results is important.

Acknowledgments

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shortwave - longwave UV Lamp Spectra I ł -= = Ξ 1 ŧ

taken directly from ultra-violet lamps at the Los Angeles County Museum of Art using a spectrophotometer. Figure 1. This graph shows the different spectra emitted by long-wave and short-wave lamps. Notice that both have a peak in the visible range, but the filtering on the long-wave is much more exclusive. Spectra

600

550

500

450

400

350

300

250

200

Wavelength

DEMYSTIFYING SILICA GEL

Steven Weintraub

Abstract

It is important to understand how silica gels vary in performance in order to select the most costeffective gel for a particular application. M_H , the hysteresis corrected buffering capacity of silica gel, is the critical variable for assessing silica gel efficiency. Calculating the correct quantity of silica gel allows for the cost-efficient selection of an appropriate amount of buffering material. If certain variables in the calculation are unknown, such as leakage rate or external RH conditions, general recommendations based on average display conditions have been provided, both for temporary exhibitions and for permanent displays. Finally, simple procedures for the use and maintenance of silica gel have been described. Passive humidity control within an exhibit case, when applied correctly, is a very simple and cost-efficient method of protecting museum collections from humidity induced damage.

1. Introduction

In 1959, silica gel was first recommended for use in museum applications as a buffering agent to control relative humidity (RH) in "closed packages" (Toishi 1959). Since that time, in spite of the use of silica gel for museum exhibition case RH control throughout the world, there has been a great deal of mystery and confusion regarding the use of silica gel systems. The purpose of this article is to demystify and explain basic information about silica gel:

- How does silica gel function?
- What are the significant differences among silica gels used in museum applications?
- How much silica gel is required to control relative humidity in an exhibition case?
- How can silica gel be reconditioned?

2. What Is Silica Gel and How Does It Work?

2.1 EMC/RH Isotherm

In order to understand how silica gel functions, it is critical to understand the concept of Equilibrium Moisture Content (EMC). Many materials contain moisture. The quantity of moisture in hygroscopic materials depends on the temperature and RH of the surrounding air. If the temperature or RH changes, the moisture content within the object will change so that it will come into equilibrium with the new condition of the surrounding air.

Moisture content is the weight of water in an object expressed as a percentage of its dry weight. The EMC is the moisture content of an object in equilibrium with a specified RH. For example, if a piece of paper weighing 100 grams at 0% RH increases to 105 grams at 50% RH, it now has 5 grams of moisture compared to its dry weight, resulting in a 5% EMC at 50% RH:

(105 g at 50% RH - 100 g at 0% RH)/100 g (dry weight) = 0.05 = 5% EMC

• To understand the moisture uptake characteristics of hygroscopic materials, a series of EMC values for the full range of RH conditions at a fixed temperature can be plotted. This is known as an EMC/RH isotherm (Fig. 1).



Figure 1. Equilibrium Moisture Content / Relative Humidity Isotherm

For organic materials, it is theoretically important to take temperature into account since it affects EMC. But, in actuality, a moderate change in temperature has a relatively small influence on EMC compared to a moderate change in RH (temperature has no effect on the EMC of silica gel within the normal range of museum use). Because hygroscopic objects are far less affected by temperature than RH in terms of impact on the moisture content and physical stability, RH is the principle focus of concern. And, since RH rather than the absolute moisture in air determines the moisture content of an object, we are concerned with RH rather than absolute humidity [1].

2.2 Buffered Cases and RH Control

The interior of a relatively airtight exhibition case will provide some level of protection against fluctuating RH conditions outside the case. However, through gradual air leakage, the RH inside

the case will slowly increase or decrease, depending on the condition of the outside RH. The rate of interior RH change depends on the amount of leakage. If the rate of air leakage is one air exchange per day, the RH within the case will equal the RH of the surrounding air within one day [2]. In reality, if there is a lot of hygroscopic material within the case, the interior RH of a case with a leakage rate of one air exchange per day will barely change. The reason for this is the buffering effect of the hygroscopic material within the case.

• As the exhibition case gains or loses humidity because of leakage, the hygroscopic material within the case must gain or lose some moisture content in order to remain in equilibrium with the RH of the surrounding air. The water gained or lost by these materials offsets most of the expected change in RH within the case. In effect, these materials act as buffers to slow down the rate of change in RH within the exhibition case.

For example, a one meter case with an internal RH of 50%, an external RH of 25% and an air exchange rate of 1x per day will lose 5 grams of moisture in a day as the internal RH decreases from 50% to 25% RH (there are about 10 g/m³ at 50% RH and 5 g/m³ at 25% RH at 22.7°C). However, if the case contains a great deal of hygroscopic material, this material will give off some of its moisture as the RH within the case falls in order to remain in equilibrium with the surrounding RH. As a consequence, the moisture given off by this material offsets almost all of the 5 grams of moisture in air lost through leakage, so the RH in the case only falls by a fraction of a percent rather than by 25% RH over a single day.

2.3 Buffering Capacity and RH Control

As a result of the buffering effect of hygroscopic materials, the RH within an exhibition case will show only a very small daily fluctuation or a very slow change in RH over time compared to conditions outside the case (Fig. 2). However, the degree of internal fluctuation or change in RH within the case depends on the buffering capacity of all the hygroscopic material within the case. If the case has a relatively small ratio of hygroscopic material compared to the total case volume, the buffering capacity of the case will be limited compared to a case with a large amount of hygroscopic material.

• In practical terms, this means that a case with a large buffering capacity may take many months for the RH to decrease from 50% RH to 25% RH, whereas if there is very little buffering capacity, the decrease may occur over a period of days or weeks. In fact, for an exhibition case where the only hygroscopic material is the object itself, the object becomes the buffer. By introducing other buffering materials into the case, it is possible to significantly reduce the rate of change of moisture from the object itself, thereby reducing risk of RH induced damage [3].



Figure 2. Annual Climatic Cycle

Since all hygroscopic materials provide some level of buffering capacity, why do museums use silica gel for this purpose rather than inexpensive, easily available organic materials like cotton? The primary reason is because of the much higher buffering efficiency of silica gel compared to organic materials [4]. Buffering capacity is based on the amount of moisture that a material will gain or lose within a specified range of RH. The buffering capacity of materials can be compared in a general way by looking at their EMC/RH isotherms (Fig. 1). From this graph, it is clear that the two illustrated silica gels have the capacity to adsorb much more moisture than natural materials such as wood, cotton or wool at the low to mid-RH range.

As a consequence of the high moisture capacity, far less silica gel is needed by weight to achieve a certain amount of buffering capacity compared to organic materials. In addition, because of the high density of silica gel (approximately 0.7 kilograms per liter or 44 pounds per cubic foot for a regular density grade), it takes up far less space in an exhibition case than an organic material with equivalent buffering capacity.

2.4 Silica Gel - A Brief Description and History

Silica gel is a chemically inert, non-toxic material composed of amorphous silicon dioxide. It has an internal network of interconnecting microscopic pores, yielding a typical surface area of 700-800 square meters per gram; or, stated another way, the internal surface area of a teaspoon full of

silica gel is equivalent to a football field. Water molecules are adsorbed or desorbed by these micro-capillaries until vapor pressure equilibrium is achieved with the relative humidity of the surrounding air. Silica gel was patented in 1919 for use in the adsorption of vapors and gases in gas mask canisters during World War I. During World War II, it was commonly used as a dehydrating agent to protect military and pharmaceutical supplies, among a number of other applications (see www:gracedavison.com/about/history.htm). Its use as a buffering agent to control RH within the mid-range rather than as a desiccant is unique to museum applications.

3. Different Types of Silica Gel - Different Types of Performance

3.1 Defining Buffering Capacity - The Variable M

The moisture adsorbing properties of silica gels are affected by factors such as capillary pore size or the inclusion of hygroscopic salts, resulting in a wide range of performance [5]. Therefore, it is important to compare the buffering capacity of different types of silica gels to determine which silica gel has the best performance for a specific application. Thomson (1977) described the specific moisture reservoir with the variable M.

• The moisture buffering capacity of a material is defined by its M value, which is the amount of water (in grams) that is gained or lost by 1 kilogram of silica gel for each 1% change in RH.

For example, if one kilogram of silica gel adsorbs 50 grams of moisture between 40-50% RH, M is calculated as follows (when calculating M from EMC values, multiply the EMC value by 10 to convert it to grams of water per kilogram of dry silica gel):

M = 50 grams of moisture/10% RH = 5

M varies because of the following factors:

- The point along the EMC/RH isotherm at which it is measured.
- The magnitude of the RH range used to determine M.
- Whether it is measured along the adsorption or desorption isotherm.
- The difference in M values derived from the adsorption and desorption isotherms (hysteresis), expressed by the variable M_H, described below.
- Whether M_H, the hysteresis compensated M value, was estimated or experimentally determined.

For example, within the range of 30-60%, the M value of regular density silica gel (RD gel) can vary from 6 to 1.25, depending on how it is calculated [6]. This large variation in M has major consequences, since the amount of silica gel required to buffer an exhibit case will vary inversely

with M. In the above example, a case would require almost five times as much silica gel if M = 1.25 instead of M = 6.

3.2 Defining Buffering Capacity - The Variable $M_{\rm H}$

To avoid confusion about the correct value of M, it is necessary to use a modified value, M_{H} , which accounts for variations in the value of M.

M_H is the average amount of water (in grams) that is gained or lost by 1 kilogram of silica gel for each 1% change in RH. This is determined by repeatedly cycling silica gel between adsorption and desorption within a specific RH range until a constant value is measured. By taking hysteresis into account, M_H reflects actual buffering performance. (See Appendix 1 for a description of M and M_H calculations.)

Three types of silica gel used in museum applications were tested to determine their M_H values in the range of 40-55% RH. [7].

Experimentally determined M_H between 40-55% RH

- RD gel = 2.0
- Art-Sorb = 4.5
- Rhapid Gel [8] = 8.7

Based on these results, RD gel is less than half as efficient as Art-Sorb, and Rhapid Gel is almost twice as efficient as Art-Sorb (Fig.3). These results are not surprising, based on the overall EMC/RH isotherms for these silica gels (Yu et al. 2001). RD gel has very good adsorption properties below 45% RH, but quickly flattens out in the higher RH range. It is very important to understand the implication of this behavior. It means that RD gel is a very effective buffer below 45% RH, but has very little buffering capacity above 45-50% RH. Art-Sorb has less buffering capacity than RD gel below 45% RH, but has a large buffering capacity above 60% RH. Its midlevel performance is between the other gels in the 40-55% RH region because this is the transition range at which it begins to improve its buffering performance [9]. Rhapid Gel has very large buffering capacity in this mid RH range because its peak adsorption and desorption capability is centered in this RH region.



Figure 3. Hysteresis Corrected EMC/RH Isotherm Between 40-55% RH

4. How Much Silica Gel Is Enough?

4.1 Too Much Or Too Little?

The most frequent questions regarding silica gel are:

- How long will silica gel last?
- How much silica gel is required?

All silica gels have an infinite life in terms of the ability to adsorb or desorb moisture. Therefore, silica gel can be reconditioned and reused indefinitely.

Recommendations for the required amount of silica gel vary from 20 kg/m³ of RD silica gel (Thomson 1977) to 0.5 kg/m³ of Art-Sorb (Art-Sorb 2003). Why are these recommendations so different? The discrepancy is not based on comparison of buffering capacity, but rather on the formulas used for determining quantity.

Thomson determined that 20 kg/m³ of regular density silica gel was required in order to buffer the
RH in an average case over a full year so that it would never require reconditioning. His goal was to create a self-correcting, maintenance-free case where the interior would be buffered against the low winter RH and high summer RH of the surrounding air (Fig. 2). (See Appendix 2.)

Although Art-Sorb does not publish the source for their recommendation of 0.5 - 1.0 kg/m³, it can be deduced from a published study by Miura (1981), referenced in earlier Art-Sorb product literature, and information referenced in the Lascaux website (Art-Sorb/Lascaux 2003). These references deal with the amount of silica gel required to offset changes in RH brought about by rapid changes in temperature, a short-term effect.

• If it is correct that Art-Sorb's recommendation of 0.5-1.0 kg/m³ is based on protection against short-term temperature effects, it is not appropriate as a basis for how much silica gel should be used within an exhibition case for protection against long-term leakage, which requires much more silica gel.

4.2 Determining the Quantity of Silica Gel

Estimating the amount of silica gel required to buffer or control RH within an exhibition case must take into account the varying condition of the display environment and the capacity of the buffering material. This can be calculated as follows:

- 1. Determine the total amount of moisture gained or lost by an exhibit case over a specified period of time.
- 2. Determine the amount of water that can be adsorbed or desorbed by a kilogram of silica gel within the anticipated RH range of the exhibit case.
- 3. The total amount of silica gel required is determined by dividing moisture gain or loss by available moisture capacity of silica gel.

These steps are encompassed by the following equation, developed by Weintraub and Tétreault (Tétreault 2003) [10]:

$$Q = (C_{eq} D)V(Nt)/(M_H F)$$

Where:

- Q = Kilograms of silica gel required.
- C_{eq} = Concentration of water vapor at saturation. (At 22.7° C [73°F], a cubic meter of air holds 20 grams of water vapor at saturation.)
- D = The differential between the external RH and RH within the exhibit case. External RH is based on the average maximum range of RH fluctuation within the room. For a temporary case, interior RH is based on the acceptable limit of the RH range within the

case. For a permanent case, interior RH is based on the RH midpoint within the case. As an example:

- For a temporary case where the internal RH range is 45-55% and the exterior range is approximately 35%-65% RH, D is the difference between the lowest internal and external RH values, 45% and 35%, or between the highest internal and external RH values, 55% and 65%. In either case, D = 10% or 0.1.
- For a permanent, maintenance-free case where the internal RH range is 45-55% and the exterior range is approximately 30%-70% RH, D is the difference between the RH midpoint within the case (50%) and the lowest or highest external RH values, 30%, or 70%. In either case, D = 20% or 0.2.
- V = The volume of the case, expressed in cubic meters.
- N = The number of air exchanges per day. (Thomson [1977] used a value of one air exchange per day for a typical moderately sealed exhibit case.)
- t = The maximum number of days that the exhibit case should remain within an acceptable range of RH (90 days for a typical temporary exhibition).
- $M_{\rm H}$ = The moisture buffering capacity of silica gel within the specific RH range of use, taking hysteresis into account.
- F = The acceptable maximum range of RH fluctuation within the exhibit case (45-55% RH as a typical value for organic materials).

As an example, the amount of silica gel required for a permanent, maintenance-free case of one cubic meter, using regular density silica gel ($M_H = 2$) and utilizing the values described in brackets for the above variables, is:

$$Q = (C_{eq} D)V(Nt)/(M_{H} F)$$

 $Q = (20 \times 0.2) \times 1 \times (1 \times 90)/(2 \times 10) = 18$ kilograms of silica gel

• Since the relationship of all variables is arithmetic, it is easy to recalculate the amount of silica gel required based on a change in one or more variables.

4.3 Quantity of Silica Gel for a Temporary Exhibition

For a short-term application such as a special exhibition that is 90 days in duration, a smaller quantity of silica gel can be used, compared to the requirement of a permanent exhibit. This assumes that the RH within the gallery space is usually moderate and rarely exceeds 35-65% (i.e. no more than 10% RH above or below the RH range within the case). If the acceptable exhibit case range is 45-55%, then the differential between internal and external RH is 10% and D = 0.1, and 9 kg/m³ of RD gel is required.

For an exhibit case located within a space with moderate RH control, the following amounts of silica gel are recommended based on their respective M_H values [8]:

Recommended quantity of silica gel for temporary exhibition cases in rooms with moderate to good climate control

•	RD gel:	9 kg/m³	or	0.55 lb/ft ³
•	Art-Sorb [11]:	4 kg/m ³	or	0.25 lb/ft ³
٠	Rhapid Gel [12]:	2 kg/m^3	or	0.125 lb/ft ³

4.4 Quantity of Silica Gel for Maintenance-Free Exhibit Cases

In addition to using the above equation to calculate the amount of silica gel required for short time periods, it can also be used to calculate the amount of gel required to buffer a case over an annual cycle, such as Thomson estimated through his "hygrometric half-time" calculation. The concept of a self-correcting maintenance-free case requires that the acceptable RH range inside the case falls midway within the annual RH range outside the case. For example, if the room RH varies from 30% to 70% RH, the exhibit case interior midpoint RH will be 50% RH. In the summer, as the room RH rises, the internal RH will gradually rise to the upper limit of its acceptable RH range, for example, 55% RH. In the autumn through winter as the room RH drops, the internal RH gradually drops back to the 50% RH midpoint and eventually to the lower limit of its acceptable range at 45% RH. In the spring through summer, the RH rises to a maximum of 55% RH and the sequence of RH self-correction continues ad infinitum.

Each period in which the humidity rises or falls above or below the RH midpoint is approximately 90 days. Therefore, the case requires a buffering capacity of 90 days. By using a value of t = 90 days and a D value based on the RH midpoint, the above equation can be used to calculate the amount of silica gel required for a maintenance-free case. In the leakage example above where t = 90, assumptions similar to Thomson's were used regarding air exchange rate (N=1), M_H value (M_H=2 for RD gel), and the RH range inside and outside the case (D=0.2). This yielded a result of 18 kilograms, similar to the value of 18.75 kg determined with Thomson's half-time formula.

Recommended quantity of silica gel for maintenance-free exhibit cases

•	RD gel:	18 kg/m³	or	1.1 lb/ft ³
٠	Art-Sorb [11]:	8 kg/m³	or	0.5 lb/ft ³
٠	Rhapid Gel [12]:	4 kg/m³	or	0.25 lb/ft ³

4.5 Margin of Safety

In reality, the rate of leakage and the actual amount of moisture gained or lost by an exhibit case is a more complex process than is taken into account either by the above equation, or by Thomson's half-time equation (Michalski, 1994). Both Thomson's hygrometric half-time equation and the silica gel quantification equation, described above, err on the side of putting in more silica gel than is actually required under specified conditions. This is because of the simplifying assumptions used to define the leakage rate. The excess gel provides an extra margin of protection. The recommended quantity also compensates for the fact that the total amount of silica gel in the case does not act instantly, especially if it is located in trays with a depth greater than a few beads.

4.6 Case Leakage

The most difficult and speculative part of the silica gel equation is the rate of leakage. At present, there is no simple inexpensive standard method for calculating leakage for museum exhibit cases. Unless this value can be quantified, an assumption of one air exchange per day is typically used. As the leakage rate increases, there is a proportional increase in the amount of silica gel required to control case RH. At a point, if the leakage rate is very high (above 2 air exchanges per day), so much silica gel would be required that passive RH buffering is no longer a viable alternative. For cases with a high leakage rate, it is essential to reduce the rate of leakage, or consider an alternative approach such as the use of an active RH control system.

4.7 Rate of Response

There is no significant difference between the rate of response of different types of silica gels during adsorption or desorption (Figs. 4, 5). The location and distribution of the silica gel are the critical factors that determine rate of response. In a space where there is no air movement, it takes approximately one day for a single layer of silica gel to fully adjust to a new RH level within a moderate range (10-20% change in RH). If silica gel is placed in a tray approximately 2.5 cm (1 inch) deep with gel, it will take much longer for the full amount of gel to equilibrate to a 10-20% RH change (approximately one month). Therefore, it is important to maximize the surface area of the gel relative to its total volume.

It is important to allow for a maximum zone of air exchange between the silica gel and the space that it is supposed to condition. If the silica gel is located in a space below the visible portion of the case, the air exchange is limited to a small slot or set of holes. Therefore, the silica gel may not effectively offset changes in RH within the display area, either from a rapid changes in temperature, or from a rapid rate of leakage. A future publication will discuss the question of air exchange and silica gel location.





Figure 4. Hours to Reach Equilibrium when RH is Changed from 40% to 55%



Figure 5. Hours to Reach Equilibrium when RH is Changed from 55% to 40%

5. Methods for Reconditioning Silica Gel

5.1 Conditioning Silica Gel Outside the Exhibit Case

5.1.1 Removing Moisture

The most efficient method of removing moisture is with heat. Although silica gel has a very high melting temperature (1600° C), it will lose its chemically bound water and hygroscopic properties if heated above 300° C. In addition, there is a new class of indicator gels, incorporating organic dyes that are heat sensitive and their color indicating dye will be effected above 125-150° C (Goldberg and Weintraub 2001). Therefore, it is not recommended that indicating silica gel be heated above 120° C and regular gel be heated above 200° C. The principle impact of a lower heat of regeneration is that a longer time is required to dry the gel and there is less potential for the degradation of silica gel properties.

In a conventional oven, the time of regeneration varies from minutes to hours, depending on temperature and the thickness of the gel. Although silica gel can be dried in a microwave oven, it is difficult to determine the temperature inside the gel. Also, since metal cannot be used in a microwave oven, only glass, ceramic or microwave safe plastic with a high melting temperature should be used to hold the gel, since the individual beads can become very hot.

5.1.2 Adding Moisture

The simplest method for conditioning silica gel is to place it in a room or environmental chamber set to the desired RH level. The best method of confirming that the silica gel is at the correct RH is by measuring the RH of a sample batch of gel. This is done by placing the sample gel in a sealed container or plastic bag with a hygrometer (use a large amount of gel relative to the surrounding air), and allow a day for the RH within the bag to stabilize with the gel mixture. Although an approximate RH value can be calculated based on weight, this method is not recommended because of its margin of error.

- Methods of speeding up conditioning time:
 - Spread the gel as thin as possible.
 - Use a fan to circulate air around the gel.
 - Periodically mix the gel layers to improve uniformity.
- For a single layer of bead, allow at least 4 days if the gel is initially dry, and longer if spread as a thicker layer.
- Silica gel can be conditioned to a higher RH than the desired level, either to speed up the conditioning process or because of the inability to control RH. If so, it is important to allow 2-3 day for the moisture to equilibrate within and between the gel beads, especially

if beads with different moisture contents are mixed together.

• The direct addition of water through mist spraying or immersion is not recommended, since the high heat of decrepitation causes silica gel beads to crack and fragment. Although silica gel retains its hygroscopic properties, the overall response time of silica gel in a tray will slow down because of denser packing from the mix of large beads and smaller fragments.

5.2 Methods for Conditioning Silica Gel Without Removing it from the Exhibit Case

Silica gel in cases can be reconditioned by adding water or appropriately conditioned silica gel to the case. This method is very effective if the silica gel is spread into a very thin layer, or has a very fast response time, such as is achieved with Rhapid Gel. Otherwise, only the upper layer of silica gel will be conditioned and there is a risk that the RH within the case will rise or fall too quickly, without adequately conditioning the full bulk of silica gel.

Increasing or decreasing surface area can control the rate of water evaporation. If there is concern about placing water directly in a case, or if a fast rate of evaporation is desired, a saturated humidifier wicking pad, preferably one treated with an antimicrobial agent, can be used. Generally, water will evaporate more rapidly in this manner because of the extended surface area of the wicking pad compared to a dish of water.

The initial speed at which dry gel removes excess moisture is very fast. It is important to limit the surface area of dry gel to prevent the case RH from dropping too quickly. This is because the speed at which dry gel adsorbs moisture is faster than the rate at which silica gel desorbs moisture.

If silica gel is conditioned in place, the rate at which the RH rises or falls within the case must be carefully monitored in order to determine if the rate is acceptable and when the water or dry gel that was placed in the case to condition the main supply of silica gel must be removed.

It is possible to calculate how much moisture must be added or removed to recondition silica gel in place (Lafontaine 1984; Weintraub 1991). It is important to take into account the impact of other hygroscopic materials inside the case. With experience, adjusting the amount of water or dry gel required may be required to compensate for other hygroscopic materials.

5.2.1 Calculate the Amount of Water Required to Increase RH

Multiply the % increase in RH required, the $M_{\rm H}$ value of the silica gel, and the weight of silica gel within the case.

For example, if the goal is to raise RH from 45% to 55% in a case containing 2 kilograms of silica gel with an $M_{\rm H}$ of 9, 180 grams of water is required:

10% RH x 9 (M_H) x 2 kg = 180 grams of water

5.2.2 Calculate the Amount of Dry Silica Gel Required to Decrease RH

- <u>Step 1</u> Determine how much moisture must be removed by multiplying the % decrease in RH required by the M_H value of the silica and the total amount of silica gel within the case.
- <u>Step 2</u> Establish the EMC adsorption value for the dry gel at the desired RH set-point and multiply this value by 10, to convert the value to the amount of moisture that can be removed per kilogram of dry gel.
- <u>Step 3</u> Divide the amount of water to be removed (Step 1) by the amount of water that can be removed by a kilogram of dry gel (Step 2). The result is the total amount required to recondition the silica gel in place.

For example, the goal is to lower RH from 55% to 45% in a case containing 2 kilograms of Rhapid Gel ($M_H = 9$). If the dry gel is a regular density silica gel (EMC = 25% at 45% RH), the amount of dry gel required is 0.72 kilograms:

1) 10% RH x 9 ($M_{\rm H}$) x 2 kg = 180 grams of water

2) 25% EMC x 10 = 250 g of moisture per kg of silica gel at 45% RH

3) 180g/250 g = 0.72 kilograms

6. Conclusion

Passive buffering of RH within the exhibition case is an important risk management tool. A wellsealed exhibition case containing hygroscopic materials will have some capacity to stabilize RH within the case. The inclusion of silica gel will enhance this effect. Silica gel can serve as a lowmaintenance method of RH control to compensate for poor RH control within the room. Alternatively, it can provide inexpensive, passive back-up when a mechanical RH control system malfunctions. Unfortunately, a lack of clear and correct information regarding how silica gel should be used and maintained has limited its use. The above discussion provides a comprehensible baseline of information on the proper and effective use of silica gel.

It is important to understand how silica gels vary in performance in order to select the most costeffective gel for a particular application. M_{H} , the hysteresis corrected buffering capacity of silica

gel, is the critical variable for assessing silica gel efficiency. Calculating the correct quantity of silica gel allows for the cost-efficient selection of an appropriate amount of buffering material. If certain variables in the calculation are unknown, such as leakage rate or external RH conditions, general recommendations based on average display conditions have been provided, both for temporary exhibitions and for permanent displays. Finally, simple procedures for the use and maintenance of silica gel have been described. Passive humidity control within an exhibit case, when applied correctly, is a very simple and cost-efficient method of protecting museum collections from humidity induced damage.

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Endnotes

1. It is possible to plot an EMC/absolute humidity isotherm, since there is a direct correlation between absolute humidity and moisture content. However, a small change in temperature will result in a much larger shift in the EMC/absolute humidity curve compared with the shift that takes place with the EMC/RH curve.

With regard to temperature and humidity control, a moderate change in temperature may not have a major, direct impact on EMC, but it will have a major influence on RH, which in turn, does have a significant impact on EMC (1° C temperature change will result in an approximately 3% change in RH at a fixed absolute humidity within the general range of 20° C and 50% RH).

2. The air exchange rate refers to the amount of time required for a complete exchange of air between an enclosed space and the surrounding air. In reality, leakage is a complicated process, and a complete exchange of air does not really take place. Air exchange is more accurately described by a half-life decay rate, typically used to explain such phenomenon as nuclear decay (discussed by Thomson, in his 1977 article on hygrometric half-time). Although less accurate, the concept of an air exchange rate is used as a standard for expressing the rate of leakage.

3. There have been a number of publications that do not recommend the use of silica gel to buffer changes in RH within a sealed environment (Sozzani 1997). The basis of concern is that the presence of silica gel can actually increase rather than decrease the change in moisture content within an object when there is a temperature induced change in RH within a sealed case. This line of reasoning does not take into account the effect of case leakage.

The primary purpose for using silica gel is to offset a loss of moisture through leakage. If there are no other buffering materials, any air exchange where there is a differential in RH between the

case interior and surrounding air will result in a direct and immediate loss of moisture content from the object. The presence of an adequate amount of silica gel will slow down the loss in moisture content from the object. Without supplementary buffering materials, there is a high risk of significant change in an object's moisture content due to leakage in a moderate to poorly sealed case. In contrast, the rather small change in an object's moisture content due to moderate temperature effects in a case containing silica gel presents minimum risk to the object.

4. A further advantage regarding the use of silica gel rather than organic materials as a humidity buffer is that silica gel is inert and does not have any inherent volatile components.

5. According to the Art-Sorb Material Safety Data Sheet (Art-Sorb/Waller 2003), Art-Sorb contains lithium chloride. Most silica gels are principally composed of silicon dioxide, with the addition of other modifiers such as aluminum to slightly alter adsorption characteristics for specific applications. Art-Sorb is the only silica gel known to contain a soluble salt component.

6. These M values were derived from data published by Yu et al. (2001). Both M values were based on the desorption isotherm. An M value of 6 was calculated between 46% and 34% RH. An M value of 1.25 was calculated between 62% and 46% RH.

7. The three silica gels tested are:

- Regular density silica gel, referred to as RD gel in this article. Regular density silica gel is the most common type of silica gel and is available from any source that sells silica gel. Because of its capacity for high moisture uptake in the low RH range, it is a very effective desiccant.
- Art-Sorb, from Fuji Silysia Chemical LTD, is a silica gel utilized in museum applications. Information is available through the Art-Sorb website (www.art-sorb.com).
- Rhapid Gel and Arten Gel, from Art Preservation Services, are silica gels specially developed and manufactured for museum applications. Arten Gel is available as an 8-mesh bead (approximately 2 mm diameter). Rhapid Gel is only available in sheet form. Information is available through the Art Preservation Services website (www.apsnyc.com).

Since Yu et al. (2001) used Arten Gel in their study, all references to Arten Gel performance in this publication are based on values from the Yu publication. Rhapid Gel values were based on research carried out by Art Preservation Services, using Rhapid Gel in bead form (prior to its inclusion in a sheet matrix).

Arten Gel and Rhapid Gel have similar EMC values at the low to mid RH range. Above 50-55% RH, Rhapid Gel has slightly higher EMC values, which improves its performance in the upper RH range.

8. In order to simplify calculations for determining silica gel quantities, Rhapid Gel's M_H is rounded off from 8.7 to 9.0 in the subsequent sections.

9. At 50% and 60% RH, there is a large discrepancy in the M values for Art-Sorb reported by Yu et al. (2001) compared to the values listed in the Art-Sorb website. The reason is based on the manner in which the values are listed. Instead of equating M values to the lower part of the RH range from which the value was calculated, it would be more correct to show the M value at an intermediate RH, or at the higher end of the RH range from which it was derived. Using the higher RH value as the basis for the M value, the value of M becomes 4 instead of 9 at 50% RH, and 9 instead of 19 at 60% RH. This approach results in M values that are in good agreement with the M values determined by Yu et al., and provides a more correct estimate of buffering capacity at the specified relative humidity.

10. Weintraub and Tétreault (Tétreault 2003) developed the equation for determining silica gel quantity, building on Thomson's hygrometric half-time formula, and a method described by Perkins (1987) for calculating the number of Gore-tex tiles required to control RH in a standard exhibit case.

11. In addition to beads, Art-Sorb is available in sheet form, containing 400 grams of Art-Sorb per m^2 (0.08 pounds per 1 ft²). Approximately 10-20 m² of Art-Sorb sheet is required to condition 1.0 m³ of case volume.

Based on their previous standard sheet size of 50×50 cm (20 inch x 20 inch), Art-Sorb recommended 5 sheets per m³ (using the formula of 0.5 kg/m³). This recommendation is not correct if the purpose for using Art-Sorb sheet is to protect against leakage. In fact, 40-80 Art-Sorb sheets are required per m³ (or 80-160 sheets, based on the modified sheet size of 25 x 50 cm currently sold in the U.S.).

12. Rhapid Gel is only available in sheet form, containing 750 grams of Rhapid Gel per m^2 (0.15 pounds per 1 ft²). Approximately 2.5-5 m² of Rhapid Gel sheet is required to condition 1.0 m³ of case volume.

In applications where silica gel bead is required for low to mid-RH range applications, Arten Bead is available and can be used as a substitute for Rhapid Gel sheet, utilizing the same 2-4 kg/m³ recommendation due to their similar $M_{\rm H}$ values.

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APPENDIX 1

1. Establishing a Value for M

Yu et al. (2001) evaluated the efficiency of three different types of silica gel, regular density silica gel (RD gel), Art-Sorb, and Arten Gel, used to control RH in exhibition cases, by comparing their M values at different RH levels. [7] According to their experimental results, M was different for each of the gels tested, and varied for a single gel type, depending on the point along the EMC/RH isotherm where it was measured. For example, within the range of 33-60% RH, they found the following variations:

M at various points along the adsorption isotherm

•	RD gel	= 6 (at 33% RH) down to 3 (at 60% RH)
•	Art-Sorb	= 3 (at 33% RH) up to 10 (at 60% RH)
•	Arten Gel	= constant at 7 (between 33-60% RH)

The confusion about varying M values can be avoided by calculating M within the specific RH range of use. Utilizing experimentally determined values from Yu et al., the average M value for the three tested gels within the adsorption range of 33-60% RH is:

M based on the adsorption isotherm between 30-60% RH

- RD gel = 4.5
- Art-Sorb = 4.1
- Arten Gel = 6.3
- Because M varies based on the range of RH within which it is used, it is important to take into account the actual RH range of interest when determining the buffering capacity or M value of a particular silica gel. [8]

2. Hysteresis and M_H

In addition to differences in M depending on the RH range of use, M also changes depending on whether the silica gel is adsorbing or desorbing. For example, when M is calculated for the three gels utilizing values from Yu's desorption range of 62-34% RH, the M values are:

M based on the desorption isotherm between 30-60% RH

- RD gel = 3.1
- Art-Sorb = 5.8
- Arten Gel = 7.4

Differences between the adsorption and desorption M values are due to hysteresis, which occurs when the EMC/RH isotherm for adsorption and desorption are not the same (Fig. 6). In order to account for hysteresis, it is necessary to repeatedly cycle silica gel through the RH range of interest until the moisture content at the top and bottom of the RH range become constant and repeatable (Fig. 7). However, if it is not possible to experimentally determine the M value within a specific RH range, it can be approximated from the silica gel EMC/RH isotherms for adsorption and desorption.



Figure 6. Hysteresis EMC/RH Isotherm for Regular Density Silica



Figure 7. Hysteresis Cycle Between 40-55% RH

For the RH range of use, the EMC for the highest RH value is taken from the adsorption curve and the EMC for the lowest RH value is taken from the desorption curve. The new hysteresiscorrected M value is referred to here as $M_{\rm H}$ (Fig. 8). This method of approximation works reasonably well over a large RH range (25% or greater) but decreases in accuracy as the RH range becomes smaller.



Figure 8. Hysteresis EMC/RH Isotherm for Regular Density Silica

The M_H values for the three gels evaluated by Yu, utilizing this method of approximation between 30-60% RH yield the following results:

Derived approximation of M_H between 30-60% RH

•	RD gel	= 2.8
•	Art-Sorb	= 3.7
•	Arten Gel	= 5 7

 $M_{\rm H}$ provides a more realistic picture of the true buffering capacity of different types of silica gels within a specified RH range of use (Weintraub 1981). According to the above numbers, RD gel is about 25% less efficient than Art-Sorb, and Arten Gel is about 50% more efficient than Art-Sorb.

3. Buffering Capacity Within the Actual RH Range of Use

The most accurate method of determining the actual buffering capacity of a silica gel in a specific range of use is to test it after cycling the silica gel within the RH range of use, as described above. A very typical RH range of 40-55% or narrower is used by museums for organic materials. Therefore, Art Preservation Services performed tests on the three silica gel types in the study by Yu et al. within this narrower range. Tests were performed on Rhapid Gel, comparable in performance to Arten Gel at the low to mid RH range, but with improved capacity in the upper RH range (see Endnote 7). The three gels were cycled at least four times between 40% and 55% RH, until the values stabilized and remained constant in subsequent runs (Figs. 3, 7). Based on these experiments, the following $M_{\rm H}$ values were measured:

Experimentally determined M_H between 40-55% RH

- RD gel = 2.0
- Art-Sorb = 4.5
- Rhapid Gel = 8.7

Based on their respective M_H values between 40-55% RH, a case would require 1.0 kilograms of Rhapid Gel, 1.9 kilograms of Art-Sorb or 4.3 kilograms of RD gel for comparable buffering performance.

APPENDIX 2

Hygrometric Half-Life

Thomson (1977) formulated a method for determining how much silica gel was required to stabilize RH throughout an entire year. He took into account that the leakage rate would permit enough moisture to enter an exhibit case during the summer to offset the loss of moisture that occurred during the winter. As a result, the extreme RH seasons would balance each other out.

Thomson assumed a leakage rate of one air exchange per day (N). Then, he took into account that leakage actually occurs gradually throughout time at an exponential rate (similar to the half-life decay rate of radioactive materials), rather than arithmetically as a single air exchange. Thus, he called the concept "hygrometric half-time". He used the following equation:

B = TN/4M $B=18.75 \text{ kg/m}^3 = (150x1)/(4x2)$

Where:

- B is the total amount of silica gel required per cubic meter of case volume.
- T is the number of days above or below the target RH (150 days).
- N is the number of air exchanges per day (1 air exchange for a typical case).
- M is the moisture buffering capacity of silica gel (M=2 for RD gel).
- 4 is based on the mathematically derived constant, 4.760, that is used to calculate the halflife rate of a material.

Based on the above values, Thomson calculated a value of 18.75 kilograms, which he rounded off to 20 kg/m³ of case volume. In the above equation, if a silica gel with a higher M value were used, the total amount of silica gel required would be reduced. In fact, in Thomson's first edition of The Museum Environment (1978), he used an M value of 3, resulting in a recommendation of 12.5 kg/m³. However, in his original Studies in Conservation article (1977) and in the 2nd edition of The Museum Environment (1986) he used an M value of 2.