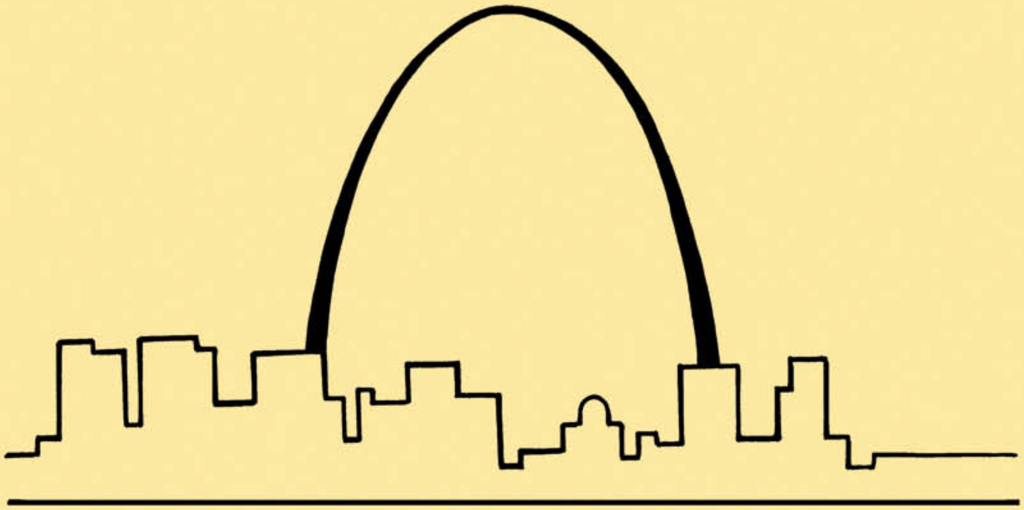
OBJECTS SPECIALTY GROUP POSTPRINTS

VOLUME SIX

1999



AMERICAN INSTITUTE FOR CONSERVATION OF
HISTORIC AND ARTISTIC WORKS

Objects Specialty Group Postprints

Volume Six

1999

Compiled by Virginia Greene and Emily Kaplan

Proceedings of the Objects Specialty Group Session
June 11, 1999
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From the 1998 OSG session:

FOREWORD

This, the sixth volume of the *Postprints* published by the Objects Speciality Group (OSG) of the American Institute for Conservation of Historic and Artistic Works, contains seven of the eleven papers presented at the 1999 OSG session in St. Louis, MO, and one paper from the 1998 session in Washington, D.C. The 1999 papers are printed in the order in which they were presented.

The theme of the 1999 OSG session was "On the Back Burner But Not Half-Baked". In my first call for papers I noted that objects conservators often have projects that end up on the back burner because other concerns take priority. Such projects include scientific technical analyses at various stages of completion, investigations into new treatments or materials, and large scale or long-term projects. There are also projects which are completed but for which there was no time to prepare them for publication. The intent of the session was to promote publication by providing a stimulus for members to write up those back-burnered projects into which went so much work and passion. I hoped that in this way some of the vast amount of information we know is "out there" would be shared with others in the field and that presentations of unfinished projects might spark interest in others who have suggestions, be able to collaborate, or begin corollary work.

The OSG *Postprints* were not published in 1998 as it was hoped that presenters would submit their papers for publication in a planned special issue of the *Journal of the American Institute for Conservation* (Spring 1999, Vol. 39, No. 1) devoted to the general theme of the meeting: "Disaster Preparedness, Response and Recovery". Several papers from the 1998 OSG session are included in that issue, but not all were submitted. We invited all authors who presented at the 1998 session in Washington, D.C. to include their papers in this volume. One paper was submitted, Constance Stromberg's "after the Fire at the Church of La Compañia de Jesús".

Of the papers from the 1999 session which are not included here, at least one, Stephen Koob's "The Toxicity of Benzotriazole: Myth and Reality", will be submitted to *Studies in Conservation*, as the paper which began the controversy was published in that journal.

I hope that this publication will serve both as a useful reference and as a departure point for further discussion with individual authors and others in the field. The papers contained herein were edited minimally, but they were not peer-reviewed and authors are encouraged to submit their papers to juried publications such as the *Journal of the American Institute for Conservation*. Authors retain all rights of reproduction of the text and images.

I would especially like to acknowledge Virginia Greene, who has been heroically editing the OSG *Postprints* since 1995, for her dedication, hard work, and sharp wit.

Emily Kaplan
OSG Chair, August 2000

THE TREATMENT OF A HAIDA TOTEM POLE: ALL THINGS CONSIDERED?

Leslie Williamson

The title of this presentation about the treatment of a Haida totem pole at the National Museum of the American Indian poses the question: were all things considered? In this project, as with all oversized artifacts, the process of evolving a treatment plan required much more time, thought, research and advice than is normal for smaller scale projects. The conservation work has been an on-going project, involving numerous conservators, contractors, and interns over a span of almost five years. The nature of the treatment itself involved drawing on the expertise of both object and wooden artifact conservators, curators, engineers, and a traditional native Haida artist. The motivation and goals for this treatment were also multifold, reflecting the necessity to move the pole several hundred miles to a new housing location, the request for exhibit, and the projected expectations of native Haida viewers. With a complicated project of this kind, it is important to continually re-evaluate the decisions as the treatment evolves, and hope that in the end all aspects are fairly considered.

The totem pole was carved about 1875 for Chief Eagle of Old Kasaan Village, Prince of Wales Island, Alaska. Heraldic poles such as this one functioned primarily as reminders of the social standing of the families who paid to raise them. They depict myths or stories that commemorate events of importance to the lineages that claimed them. The village of Old Kasaan was established in the 1700's when the Kaigani subgroup of Haida moved from the Queen Charlotte Islands and took over part of the Prince of Wales Islands from the Tlingit. Many village sites were somewhat unstable, because groups moved with changes in allegiance and changes in resources. Around 1880, Chief Son-I-hat of Old Kasaan built a new clan house at a site near a cannery that would be called New Kasaan, and by 1900 his people had basically deserted the old site. Many of the house fronts and poles of the old village were subsequently given away, sold, or taken.

One of the earliest efforts to salvage poles came from a relationship of the Alaska territorial governor John Brady and the Kaigani Haida. In 1890 a dozen or so poles, including some from Old Kasaan, were given to Brady and eventually became the Sitka National Historic Park. Preservation was attempted in the 1930's, when the Civilian Conservation Corps (CCC) had a program to salvage poles, and several were moved from Old to New Kasaan. Along with the removal and relocation of poles by the CCC, attempts were often made to recarve old poles to preserve their forms. These carvings often proved unsatisfactory, leading to heavy repainting with little relation to original color schemes.

When the nephew of the last chief with claim to the pole in this project died without a successor, the pole was sold from the village to provide money for a burial feast for the chief. Unfortunately the feast was never held The pole was acquired by the Museum of the American Indian (MAI) in the late 1930's. The pole was erected outdoors in front of the MAI on upper Broadway in New

York City in 1941, and remained there with periodic repair and repainting until worries about the security of exhibiting it outdoors in a changing neighborhood led to the lowering and transfer of the pole to a storage flat on blocks outdoors at the MAI's storage facility in the Bronx in 1982. For a few months in 1984 the pole was exhibited in the atrium of the IBM building in New York, and a small amount of surface restoration occurred at that time. Following this the pole was returned to flat storage in the Bronx.

In 1994, new covers were installed over the museum's four totem poles, and at that time thorough condition examinations were conducted to establish their feasibility for use in exhibits as well as their general needs for shipment and storage at the museum's new storage site in Suitland, MD. James Hay of the Canadian Museum of Civilization (CMC) was contracted for this evaluation, utilizing his considerable experience and expertise gained from treatment of his own institution's totem poles. His assessment was that the Haida pole was in relatively good condition when compared to our other poles, but was still in rather poor condition overall.

As is common with most totem poles, it was not carved in the round, but rather hollowed out along the length of the back to reduce weight and splitting. Examination revealed that a modern fir support pole had been affixed to the lower 2/3 of the hollowed back by means of iron bolts and an iron collar, all heavily corroded. The eagle figure, at the very top of the pole, was found to be made of an entirely separate piece of carved cedar, inserted into the curve of the main pole and attached with 3 iron bolts extending through to the front of the potlatch rings and 3 banding straps around the entire assemblage holding it together. The bolts were very corroded, and there was extensive rot around the attachment area. There was also another separately carved piece of a hunter figure that belonged at the bottom between the legs of the lowermost beaver figure but was detached completely. There were significant areas of longitudinal cracking at both the top and bottom of the pole that were quite unstable.

The other concerns for the pole were cosmetic, ranging from numerous small losses filled with modern repair materials like cement, chicken wire, putty, and non-cedar wood affixed with various kinds of hardware, to many, many layers of overpaint. Mr.Hay's experience with removing paint from aged cedar surfaces indicated it would take thousands of hours and still may not have provided an acceptable surface. His final recommendation was that the pole was in good enough condition to be moved horizontally with proper support, but could not be safely erected without repair and additional support, and would need to have either extensive and painstaking paint removal or additional overpainting if the modern color scheme was desired to be corrected.

At this point, the curatorial and exhibits departments decided that they might want the pole to stand in the entry way of the future museum, so plans for treatment of the pole were formalized. During the time of this evaluation and planning the project was being overseen by the head of conservation, Marian Kaminitz, and by former staff conservator John Moses, who directed all the testing, planning and work for the first year of the project before his return to Canada. I inherited the project in 1995. Following the recommendations of Mr. Hay, the treatment was planned to address the structural needs first, to be followed by the surface needs.

First, a tent-like enclosure was constructed over the pole to provide a sheltered work space, since at 43 feet the pole was too long to fit in available indoor space. To address structural instabilities at the top and bottom of the pole, the fir support pole on the lower two-thirds was removed. Then the attached eagle figure was removed, to allow access to the large, unsupported cracks near the top of the pole. There was extensive loss of wood from rot around the upper crack, probably accelerated by organic matter trapped between the back of the pole and the eagle figure.

The crack was joined with 3 inset butterfly joins adhered with bulked epoxy resin. A large volume of new cedar was carved in layers and adhered in the loss areas around the crack, from the back and then the front, to provide a sound area for attachment of loose surface pieces and the eventual reattachment of the eagle figure. The crack at the bottom was not repaired directly, instead it would be secured with a new custom made support frame we called the "strongback". The strongback design was used at the CMC, having been developed by Mr. Hay with help from engineers and steel fabricators, to provide a framework and lifting point for erecting the pole and to provide a means for securing the pole to the building structure once standing. In our case, it would also be a means for bridging the lower crack, with a curved internal support.

To build the strongback we again contracted with someone with previous experience, Maurice Dulepka, who had provided similar supports for poles at the CMC. Mr. Dulepka came to the Bronx in the Fall of 1996 to assess the pole and make measurements, and proposed using a design with a stainless steel hollow square mast running up the middle of the back of the pole, with extending ladder-like arms to attach to the back edges of the sides of the pole.

We also invited Jim Hart, a prominent Haida carver from Masset, BC, to consult with us on the direction the rest of the project would take. With the issues of basic structural integrity resolved by the strongback, the remaining concerns were more subjective in nature and we wanted input and direction from a knowledgeable native perspective. We asked him to help us determine what a contemporary Haida viewer might expect from seeing this pole on exhibit, with the hopes of incorporating his expectations and requests into any surface work that might be done.

Having Mr. Dulepka and Mr. Hart consulting at the same time had an added benefit in helping resolve some crucial issues. We had planned to bolt the separate eagle figure back in place using pre-existing bolt holes, and to connect it directly to the strongback for security. According to Mr. Dulepka's measurements, however, connection of the eagle to the strongback was going to be awkward because the back of the eagle extended beyond the plane of the hollow steel mast. Mr. Dulepka wanted to remove wood from the back of the eagle's post to make it flush with his steel structure, allowing for a stronger connection.

We were hesitant to remove anything significant from the pole, but Mr. Hart was able to provide some background to justify it, or at least reduce our worries over having some wood removed.

His estimation was that the second piece of wood, attached to the top of the pole, could not be original. He said that if the upper bird figure had deteriorated away while the pole was in the village, the owner would never have had a replacement figure carved and added after the pole had been raised: it just "wasn't done". We can see in photos of the pole in situ in 1924 that an eagle figure does exist at the top of the pole, but that it looks fairly degraded, with vegetation growing from it and no beak present. We can also see in photos from just after the time of removal of the pole from the village in the 1930's that a different eagle figure is present, with a slimmer body and head, and a protruding beak, which is how the pole looked upon acquisition by the museum. Therefore, while the current eagle is original to the time of acquisition, it is actually out of keeping with the traditional lifetime of the pole. We discussed removing the eagle figure completely, or having Mr. Hart recarve a top more in keeping with the quality and style of the original figure, but in the end it was decided to keep the existing addition as important to the history of the pole. Considering Jim Hart's views, and the necessity of achieving a secure attachment, it was agreed that it was acceptable to remove a few inches from the back of the lower part of the eagle figure, which he did for us with his own carving adze.

After this final step in planning the structural support, Mr. Hart helped devise the surface treatment during discussions with curator Mary Jane Lenz, James Hay, myself and a number of interns and fellows. Again, his opinion was that traditionally, once a pole had deteriorated to a certain point, it wouldn't have been repaired, it would just have been left to continue to deteriorate and perhaps a new pole would then be erected. Our situation, though, was different from what would happen on site in a native community. We had an historic pole that had been removed from its context, that we wanted to preserve and show as an example of 19th century carving. Mr. Hart felt that just because the maker wouldn't have thought of preserving the pole didn't mean we couldn't or shouldn't. He didn't find it objectionable to exhibit the old pole, and even though there has been a resurgence of Haida artists making high quality carving who could carve us a replica or a new pole, he thought the pole could have a place to teach about the history of the Haida.

Mr. Hart did object to showing the pole in its damaged and misinterpreted state. Because the totem pole was a representation of the status of a person or family, a deteriorated pole would be replaced by a new one as a point of pride and to show ongoing prosperity. He thought that for us to show a pole that appeared to be in poor condition would not be well received by Haida viewers. He didn't want us to make our pole look new again, but just good enough. It needed to have clearly readable forms, because you have to be able to distinguish the characters on the pole in order to "read" the story. Also, the surface coloration had to be accurate. The Haida use a simple and predictable color scheme, which the pole did not resemble. For him, the pole in its current state didn't look Haida. He asked that we replace poorly made old fills, and insert wood in any rotted or lost areas that interrupted the lines of an important edge or area that defines a form. Especially disturbing was the beak on the eagle, which was obviously an even later addition, and didn't reflect the correct shape of an eagle's beak. Mr. Hart provided us with a detailed listing of areas he found in need of work, and also made a sketch of the generally appropriate color scheme for this kind of Haida pole.

The next spring, the strongback was installed on the pole, with the assistance of Mr. Dulepka and Mr. Hay. Throughout the summer, we proceeded to fill the areas designated by Mr. Hart with carved blocks of cedar. Surfaces were left a little proud, allowing for final surface finishing by him. We asked Mr. Hart to do the final carving, because in many areas the exact shapes were unclear to us, but to him, with a lifetime of studying and carving traditional Haida forms, they were obvious. Equally obvious was the vast difference in carving skill between us and him. We also sampled to try to find original paint colors, and tested methods for removal of the modern paint. Neither proved successful, and we concluded that toning and overpainting the existing paint using an isolating layer of methyl cellulose and gouache would be more time-effective, satisfying, and less damaging to the underlying wood.

When Mr. Hart returned in the Fall of 1997, he provided the eagle with a new beak, and finished carving all our fills, giving them a faceted, shimmering surface we could never have achieved. He also approved a palette of gouache colors including red and black for basic forms on the eyes, brows and lips, and a neutral grey to try to better mimic the color of unpainted aged cedar. To avoid running or fading of the colors, the repainting was not done at the time and will be done once the pole is transported to indoor storage. We hope Mr. Hart will come back to oversee and assist in that work.

Finally, this ongoing project is drawing to an end. The transportation of the pole to the museum's new storage building in Suitland, MD, is planned for late 1999. After all pest management procedures are completed and the pole is loaded on a truck, the direction of future work will fall to the permanent conservation department staff working at the storage facility in Suitland. This juncture in the phases of the treatment of the totem pole provides the opportunity to try to evaluate the entire process, to determine once again if all things were indeed considered. This is a necessary practice since with any project that stretches over a long period it is easy to lose the overall focus of the work while being involved in it .

As a means to this evaluation, I questioned a number of the people involved in the project to see how they now view our overall results. When asked if he would have treated the pole differently if it had been at the Canadian Museum of Civilization, James Hay offered only that they would have worked indoors, which would have allowed for year round work, but also noted that our outdoor tent, with fresh air and picnic tables nearby, was quite pleasant. He did elaborate on his enjoyment of working with Jim Hart, and compared it to his previous experience working with Kwakiutl artists Bruce Alfred and Doug Cranmer as consultants on their treatment of the Wakas pole. He applauded our decision to have someone from the original community as a principle decision-maker in how that material should be displayed, and felt that aside from it being good policy, it will avoid having any questions on authenticity of the treated artifact. John Moses, the original project conservator, similarly supported the process we used, summing it up nicely as: 1. Utilizing available conservation expertise to address structural issues, 2. Utilizing available rigging and construction expertise to ensure proper loading and stabilization for transport and reinstallation, and 3. Utilizing native expertise to confirm appropriate design and structural elements, and to work alongside conservators to complete this work.

There were many decisions made throughout this project, and most of them required combining a number of viewpoints to reach a compromise answer. Probably no one thing was absolutely wrong or right, but this is of course often true in conservation. Certainly with an artifact of this size no decision was ever taken lightly. In this project the attempt was to balance the basic needs of conservation of the pole, the institutional needs for display, and the culturally based visual needs of the Haida. We hope a satisfactory balance of them all was reached. Undoubtedly the inclusion of so many skilled and knowledgeable people in the process was invaluable, and ensured that the best of each person's ideas were incorporated. The hard work and good humor of the numerous individuals involved was a great asset and greatly appreciated.

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Figure 1. Pole, showing modern repainting, installed in front of the Museum of the American Indian, 155th Street and Boadway, New York, circa 1963. The repainting subsequently weathered off.

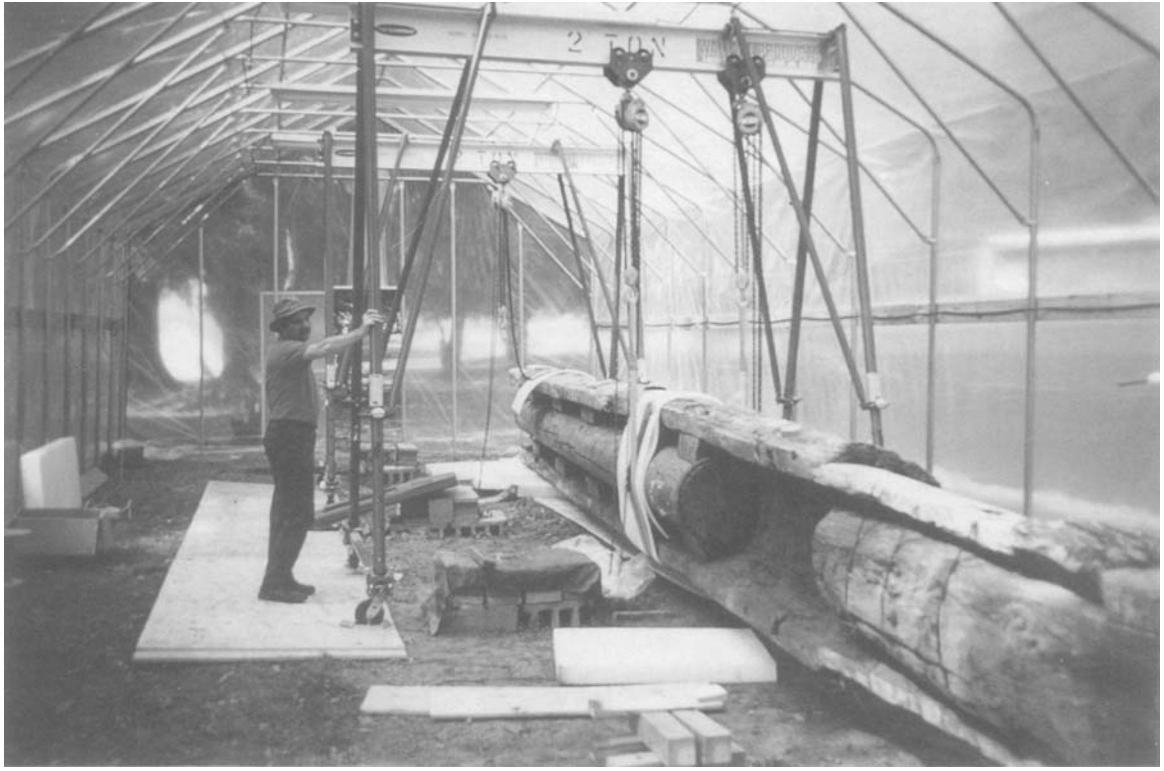


Figure 2. James Hay inspecting the back of the pole, with the old support pole visible at the far end and the eagle figure with old metal banding straps at the near end.

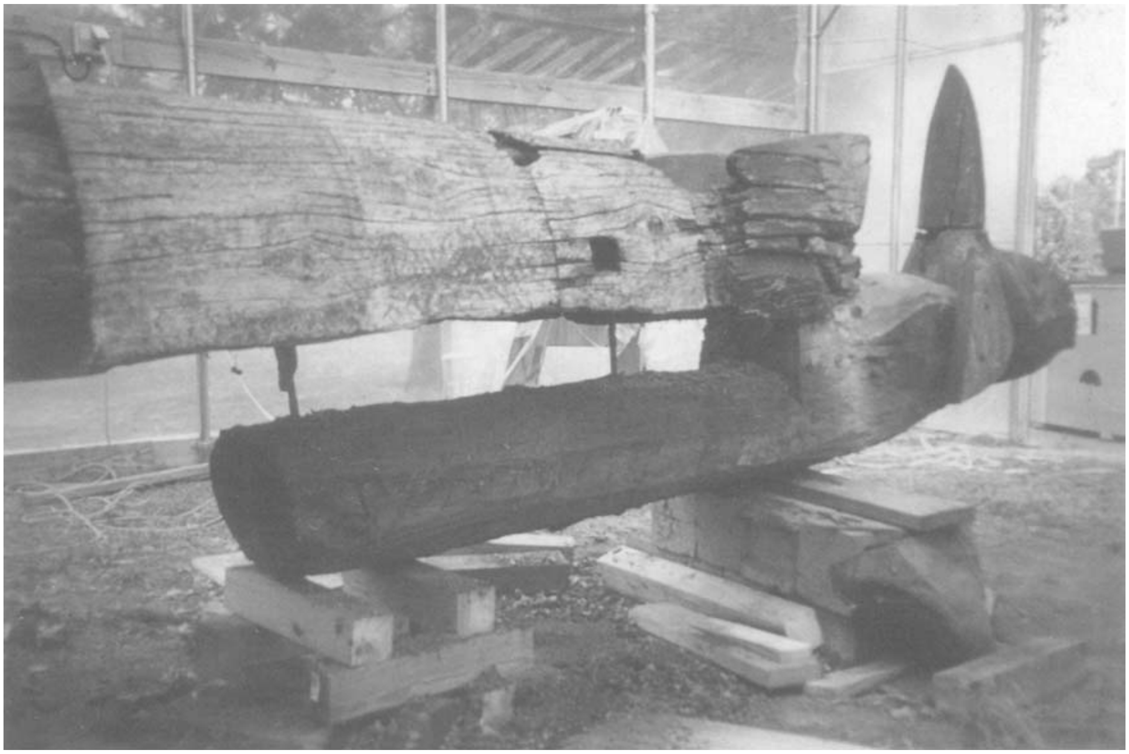


Figure 3. Eagle figure being lowered away from the pole to gain access to cracks and rot.

Figure 4. The pole and the strongback, prior to attachment.

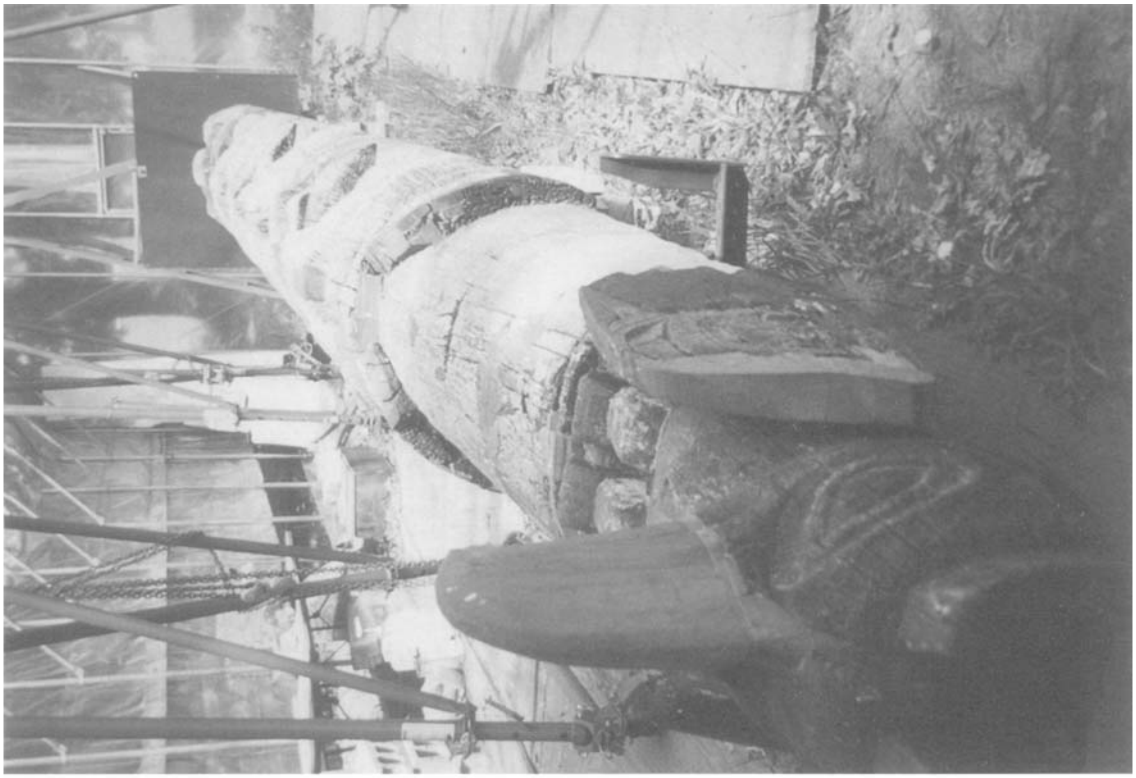


Figure 5. The pole mounted on the strongback, with all wood fills complete.

CORROSION INTERCEPT® TENT PACKING AND HANDLING SYSTEM FOR DONALD JUDD'S BRASS AND COPPER SCULPTURES: EXPERIENCES WITH PACKING AND HANDLING METHODS

Eleonora Nagy

Introduction

This paper discuses the latest result of our experiments at the Solomon R. Guggenheim Museum with various packing and handling systems for Donald Judd's brass and copper sculptures.

In the course of the last 30-some years, Donald Judd has emerged as a pivotal figure in the creation of a fundamentally new attitude toward the art process. Referred to as minimalism, this new approach rejected any reference to subject matter or the artist's emotions. It demanded a new way of defining what art is, and set forth a new philosophical base and a non-subjective aesthetic.

Judd, more than any artist before, explored and appropriated the wide range of industrial techniques and materials made available only in the last few decades of industrial evolution. His sculptures were made, or rather machined to specification, by a fabricator of industrial sheet metal products, using highly polished industrial brass and copper sheets. By providing drawings and precise measurements only for a fabricator and not building any of his works himself, Judd emerged as one of the pioneers erasing the artist's hand in the creation process.

Composed of immense, geometric shapes, Donald Judd's minimalist sculptures epitomize simplicity and perfection. The repeated identical units, free standing, in vertical stacks or horizontal progressions, display the characteristics of Judd's sculptures: flawless, highly polished, uniform surfaces of impeccable construction, meticulously executed precision, cleanness. Parts are repetitive, often equal and uninflected. A fusion of surface, substance and color takes place without the sensation of gravity. Juxtaposed with the highly polished metal, Judd often used sheets of vibrant colored Plexiglas.

The precise and uniform construction and the physical perfection are obvious qualities – so obvious, that people tend to forget how crucial they are to the work's visual power. One becomes painfully aware of the high degree of finish and the delicate use of materials when a work is damaged. In most traditional art, a small blemish can be absorbed or masked by the complexity of the compositional arrangement and by the variations on the surface. Minimalist art, in this respect, is much more vulnerable. In Judd's case, the slightest scratch or stain on the surface seriously jeopardizes the work. The damage destroys the work's visual consistency.

Since 1959, Judd was an articulate writer and extensively discussed many of the most pertinent issues of his art. Judd maintained that a natural and even tarnish layer on his sculptures was acceptable, but the slightest accidental damage, a dent, a scratch, fingerprint or stain would destroy the material beauty and impeccable uniformity, and therefore the legacy of the sculpture. Also, Judd clearly expressed his disapproval in applying coatings on his metal sculptures. This legacy of Judd's severely impacts conservators who are responsible for the preservation of his artwork. Local repair of a small damaged area is nearly impossible without losing the meticulous uniformity and perfection of the surface. Often the entire surface of a sculpture has to be addressed for treatment any time the slightest damage occurs. With demanding exhibition schedules, treatment of these large scale and fragile surfaces is arduous and exorbitantly expensive. Conservators lack reference and established guidelines that define treatment of contemporary copper alloy sheet metals.

With Judd's sculptures, the need for a conservator's intervention most often stems from circumstances such as improper handling, installation, packing and storage. To prevent interventive treatments, such as re-polishing of the surface by the fabricator or the conservator, it is important to focus on packing and handling. The Guggenheim Museum has concentrated on preventive measures that have resulted in a packing system allowing handling of the sculpture from storage to installation without touching the surface of the works. It avoids direct contact of any packing material with the surface of the sculpture, and provides an enclosed controlled environment for the work in storage.

Before the system is presented, a few examples of various experiences will be discussed and new materials used in the system will be introduced.

Damage from Handling and Packing

It is well known that touching any highly polished brass or copper surface with bare hands will result in local tarnishing, which in the course of time, will etch into the metal. Almost without exception, in museum practice gloves are used. As latex and nitrile gloves may emit some volatiles or leave residues, generally cotton gloves are preferred. In the heat, sweat and effort of an installation, however, perspiration through the cotton gloves can be noticed. Perspiration marks usually last for a few seconds after the work is handled. This situation can be improved by a double glove method, by using a cotton glove over a latex one. Eliminating perspiration marks from the hands only drew our attention to the fact that other parts of the body, such as face, neck or lower arm occasionally come into contact with the metal surfaces. Handling larger sculptures and units with wrist-length gloves allows the bare lower arm to contact the metal. After these observations installation crews were asked to wear long sleeves.

The packing materials encountered in the past that were in contact with the surface of the sculpture have presented some problems. For example, Polyfoam™, a thin polyethylene foam, wrapped and secured with an ordinary paper masking tape leaves marks on the surface of the metal if the work remains wrapped for a long period of time. The wavy pattern from the Polyfoam™ transfers to the metal. The tape, though not in direct contact with the metal surface, off gases and the sulfur from the masking tape leaves a clearly distinguishable blackish line on the surface.

Volara™, also a polyethylene foam, leaves the copper surface dark when it is in direct contact with the metal. The wooden storage crates, cushioned with Volara™ lined Ethafoam™ bumpers (Figure 1) were newly made, exactly one year before the date the damage shown in Figure 2 was noticed.

We have tentatively identified wrapping materials as the cause of the following surface marks: a straight disfiguring line across the surface of *Untitled 1973*, shown in Figure 3, and a startling pattern shown in Figure 4. The straight line in the first example (Figure 3) may be related to straight edges of wrapping papers. In the second example (Figure 4), contact with polyethylene sheet or a similar moisture barrier material is the suspected cause. Cotton twill tape or fabric placed in direct contact with the metal surface may leave transfer marks on metal surfaces. Transfer marks from contact with twill tape (Figure 5) and a cotton/polyester fabric were noticed on a contaminated copper surface after a year of storage. Consequently, materials that are normally considered archival have been found to leave disfiguring patterns on the brass and copper surfaces.

Corrosion Intercept®

The main cause of atmospheric corrosion of non-ferrous metals is the presence of sulfur and/or chlorine contaminants in the air. If these elements are eliminated from an enclosed environment containing the sculpture, the problem of maintaining the sculpture in pristine condition could be solved. The option became feasible by adopting a product called Corrosion Intercept® from the industrial market.

In the early 90's AT&T developed a product named Corrosion Intercept® to provide protection of non-ferrous metals from corrosion caused by atmospheric hydrogen sulfide, carbonyl sulfide, hydrogen chloride and other constituents. This brown, thin, heat-sealable barrier sheet is a polyethylene film which incorporates a semi-conductor (copper) that is covalently bonded to the polymer. The sheet is a lamination of three layers that are extruded at 280° F, and fused together without an adhesive. The polyethylene core layer provides the strength, and half the thickness of the sheet. The remaining two solid Intercept layers sandwich the polyethylene center. The Intercept component acts as a preferential corrosion site (sacrificial anode), whereby the covalently bonded copper additive becomes the sacrificial agent. The captured contaminants bond permanently with the additive and create stable bonds, thus leaving the object inside a Corrosion Intercept® sheet protected and unaffected by corrosive gases. Intercept does not contain volatile additives, so it does not contaminate the works it is used to protect. It does not need to contact the object to provide protection. When Corrosion Intercept® becomes ineffective and saturated with contaminants, the brown foil turns black, but does not release any contaminants to the

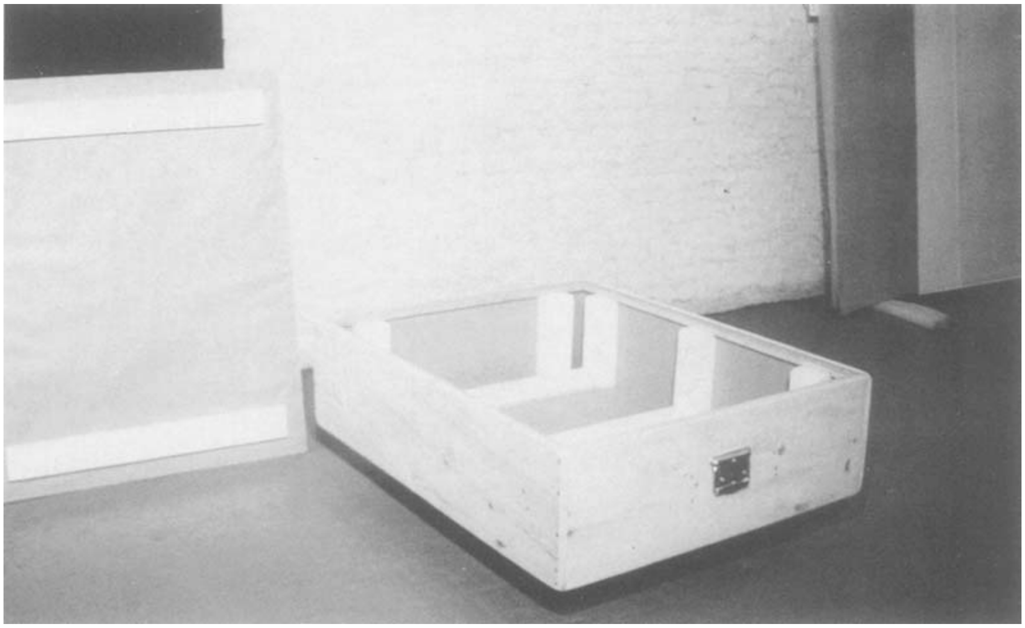


Figure 1. Storage crate, cushioned with Volara lined ethafoam bumpers for D. Judd: *Untitled 1969*, “Copper Stack”.

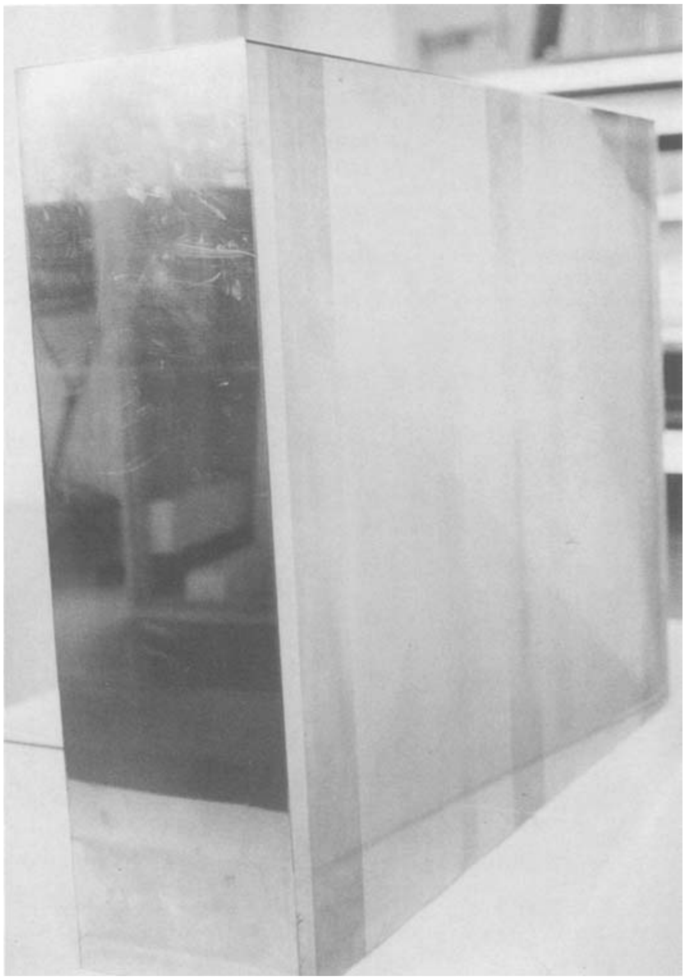


Figure 2. Dark lines on the object (Judd: *Untitled 1969*, “Copper Stack”) where it was in contact with the Volara bumpers.

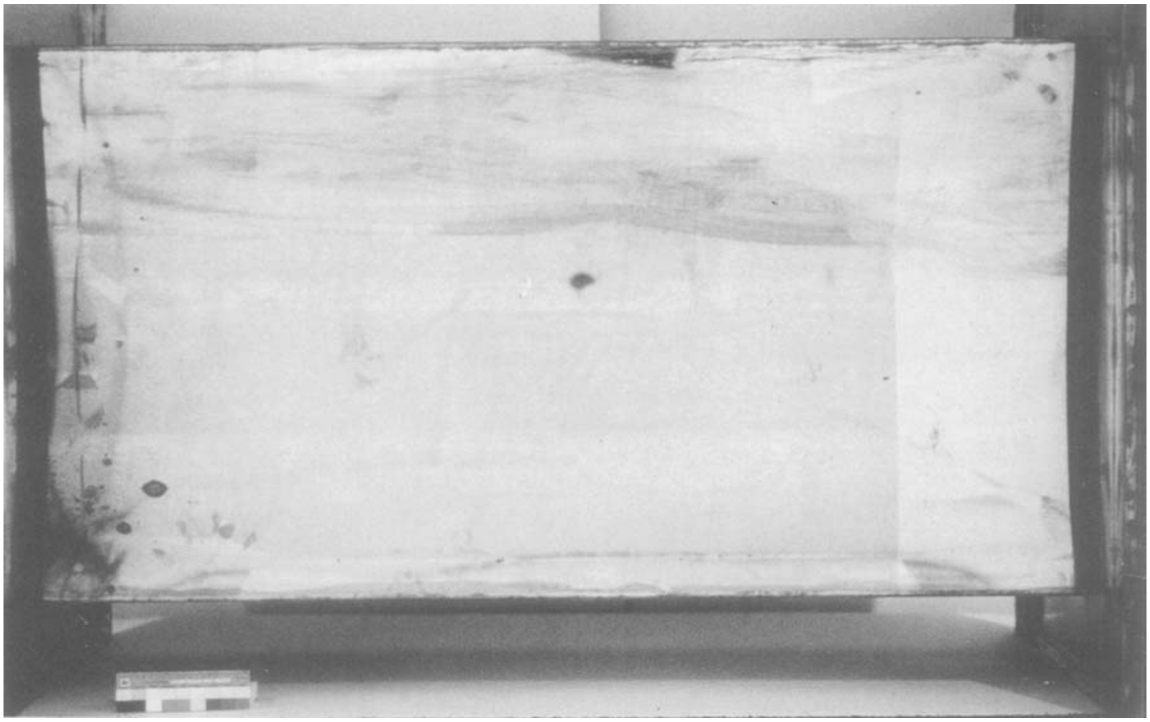


Figure 3. Straight lines of tarnishing on D. Judd: *Untitled 1973*, possibly from wrapping materials in contact with the surface.

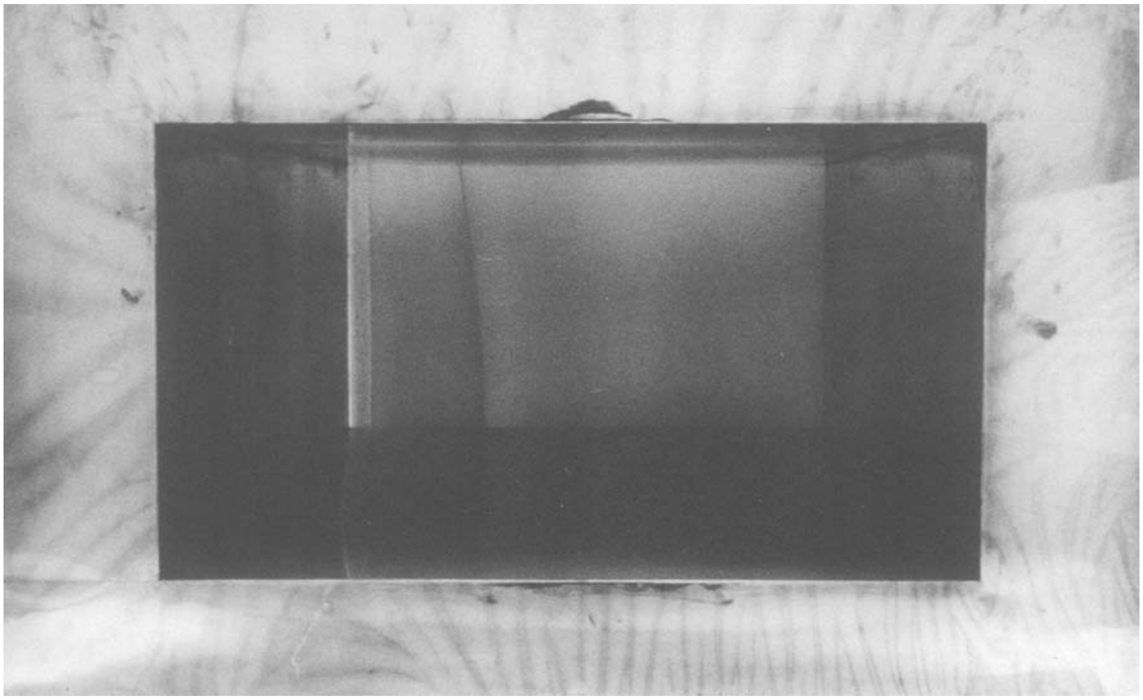


Figure 4. Pattern on the surface possibly from contact with polyethylene sheet. D. Judd: *Untitled 1973*, brass.

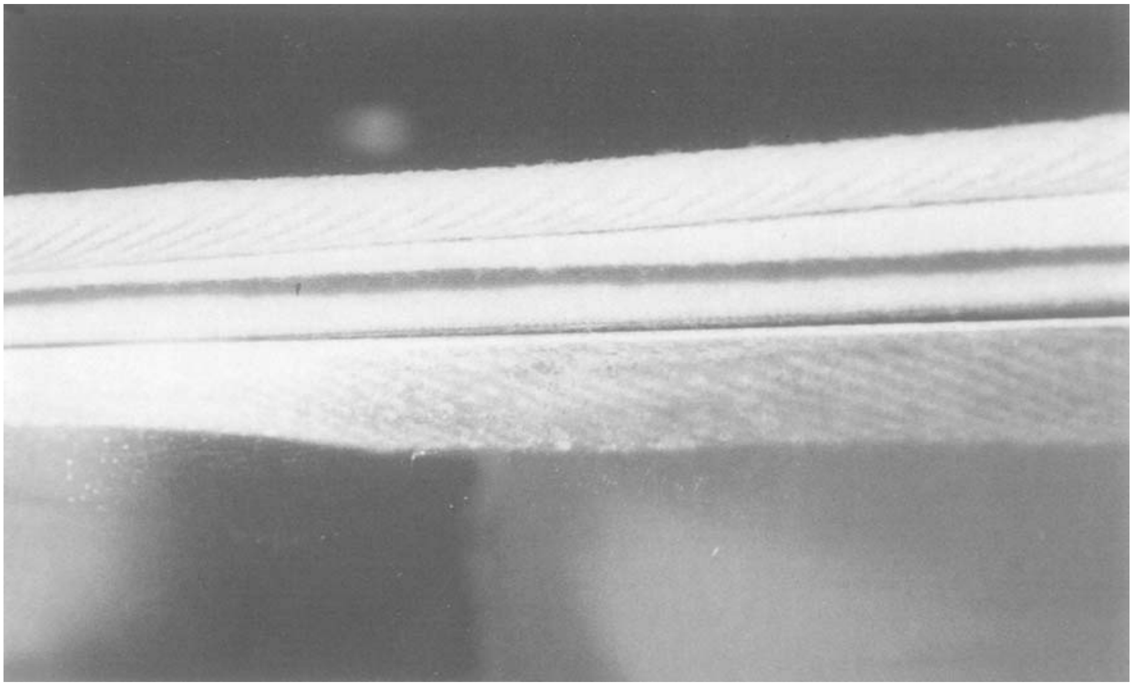


Figure 5. Transfer mark from twill tape on copper surface after one year storage. D. Judd: *Untitled 1969*.

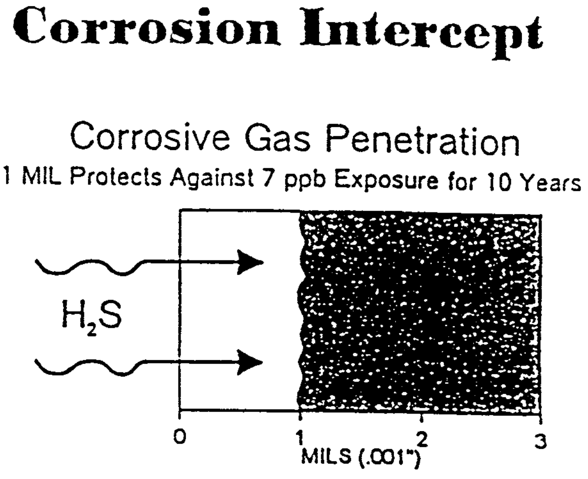


Figure 6. Source: "Inhibition of Metallic Corrosion by Reactive Polymers" in Bell Labs, *Technical Memo 11545-871009-17*, 11-12-1987. Permission by John Franey, co-author and member of Technical Staff, Lucent Bell Labs, Murry Hill, NJ.

surrounding environment. Based on testing done at Du Pont and AT&T it was determined that under average industrial levels of atmospheric sulfur and chlorine, it would take over 10 years for sulfur or chlorine to break through a 0.001" thick film (1 mil) of Corrosion Intercept® (Figure 6). Because the urban indoor environment has approximately 10 times lower average sulfur level than industrial environments, the life expectancy of a 3 mil Intercept in a museum environment can easily be expected well over 30 years (Figure 7). Results of corrosive gas protection of copper with the Intercept are published by the same company and are shown in Figure 8. Two commercial industrial corrosion inhibitors, Benzotriazole (BTA) and Imidazole (IMDA) were tested against Corrosion Intercept® at 5 ppm sulfur exposure, showing significantly better performance of Intercept as compared to the other tested materials. The water vapor permeability of an Intercept film is less than half that of a polyethylene with the same thickness (Figure 9). The price of Corrosion Intercept® is about the same as regular polyethylene sheets and can be purchased in the form of sheets, bags, corrugated board and other forms, in different thickness ranging from 2 mil-8 mil. The reactive polymer can also be formed into tubes, bubble pack, trays etc.

Previous Packing Experiences using Corrosion Intercept®

For six years the Guggenheim has been monitoring sculptures packed in Corrosion Intercept® sheet. The entire surface of the sculpture was wrapped first with a pre-washed cotton/polyester fabric followed by Corrosion Intercept®. Sculptures in pristine condition that were packed with this method have not changed their appearance in 6 years. As an example, Figure 10 shows a Copper progression which has been stored at the Guggenheim Museum with the pre-washed cotton fabric and Intercept wrapping system for 6 years. The piece was wrapped in pre-washed cotton fabric, then wrapped in Corrosion Intercept® and taped with an acrylic adhesive tape (Figure 11). As described in this example, sculptures can be adequately protected by simply wrapping them in the Intercept sheet, making sure that the edges of the Corrosion Intercept® sheet overlap. Alternatively, the edges can be sealed using a common, household vacuum–heat sealer. For this version, it is suggested to design an oversized bag, so the bag can be re-sealed and re-used a number of times. Experience at the Guggenheim Museum indicates that Corrosion Intercept® effectively protects the sculptures from pollutants in addition to being practical and economical. However, wrapping in fabric followed by Corrosion Intercept® was only successful for objects packed in pristine clean condition; a requirement no museum operating on a tight budget and exhibition schedule can afford. The metal surface had to be protected from contact with hands or wrapping materials and combined with the protection of Intercept.

Corrosion Intercept® Tent Packing and Handling System

The latest result of our experiments, the Corrosion Intercept®Tent Packing System, avoids contact with any surface of the sculptures. To understand the nuts and bolts of this system, it is helpful to first explain the construction method of Judd's sculptures.

Untitled 1972, shown in Figure 12, consists of six seemingly simple three-dimensional forms. The six identical cubes are equally spaced, forming a horizontal stack on the wall. Each cube is fabricated from two sheets of 1/16-inch sheet brass. The larger of the two sheets is bent twice to form the top, face and bottom of the cube. A smaller, separate sheet forms the back of the cube (Figure 13, left) When viewed in a cross section from the side, it is apparent that the larger sheet forms a big "U" into which the smaller "U" of the back sheet is inserted. The two sheets are joined, and form a double-sheeted lip along the top and the bottom of the cube. The reinforced lip along the top also functions as a hook to hang the pieces on the wall. Typically for Judd's sculptures, these lips hang on a galvanized sheet metal cleat that is attached to the wall (Figure 13, right).

Imagine a wall installation of a cube, with the lips secured to the wall, then rotate the image 90° degrees counter clockwise (Figure 14). The wall becomes a horizontal storage tray and the lips, secured to the cleats of the wall will be secured to the tray by clamps. The cubes, being secured with clamps to their tray, allow moving and transportation of the sculpture without touching it. A tent can be secured to this a tray, as illustrated in Figure 15, thereby creating a sealed microenvironment against pollutants.

For installation, the tent is taken off (Figure 16). A second tray, called the installation tray, is placed alongside the bottom of the cube, in contact with the bottom surface of the sculpture. The installation tray is secured to the storage tray. Holding on to the 2 trays, the work is rotated 90° degrees, to the vertical position it will hang on the wall. After the clamps of the storage tray are undone, and the storage tray is taken away, the work is properly positioned and prepared to be lifted up by the installation tray to be hung on the wall.

For de-installation the procedure is reversed. Using this system no handling of the work by hand is necessary. During the entire installation procedure only the bottom of the cube comes in contact with a packing material, and for no longer than 10 minutes. The only time the work has to be touched by hand is when the system is newly made and the work is placed for the first time on its new storage tray. Unless a conservation treatment requires complete dismounting of the object from its packing system, the work can be installed, de-installed, transported long distance and stored long term without touching the surface and thereby avoiding uneven tarnishing and corrosion.

Now let us go over a detailed step-by-step description of the system. First, a plywood tray 6 inches larger on each side than the footprint of a cube was made (Figure 17). Three inches are allowed for the inner space of the tent and three inches to secure the rims of the tent to the storage tray. The two long clamps, along the top and bottom lips were made of Masonite and plywood. The clamps glide out to lock, and in to open in two grooves which are secured with screws from the bottom of the tray (Figure 18). The top of these screws must be embedded into the surface of the clamp and covered. This precaution will avoid scratching the object accidentally with the top of a screw.

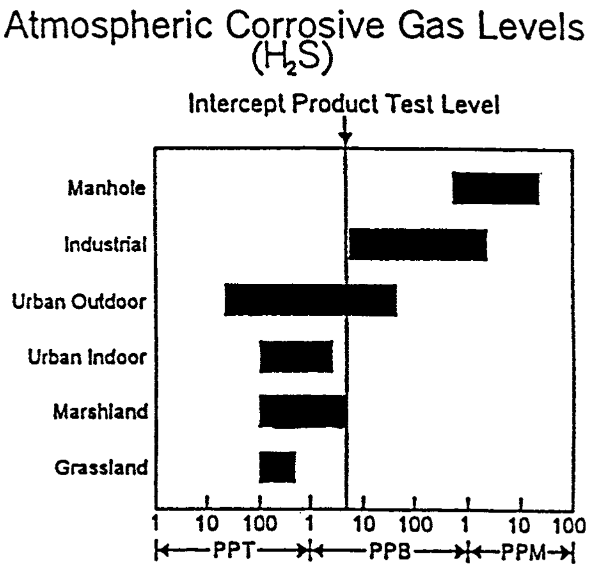


Figure 7. Source: Graedel, T.E.: "Concentrations and Metal Interactions of Atmospheric Trace Gases Involved in Corrosion", Reactive Polymer Presentation, Baxter Industrial Seminar, *International Congress on Metallic Corrosion*, Toronto June 3-7, 1984, pp 396-401. Permission by John Franey, co-author and member of Technical Staff, Lucent Bell Labs, Murry Hill, NJ.

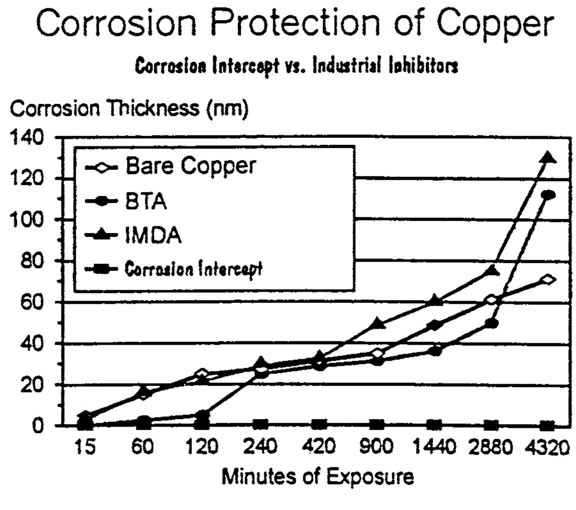
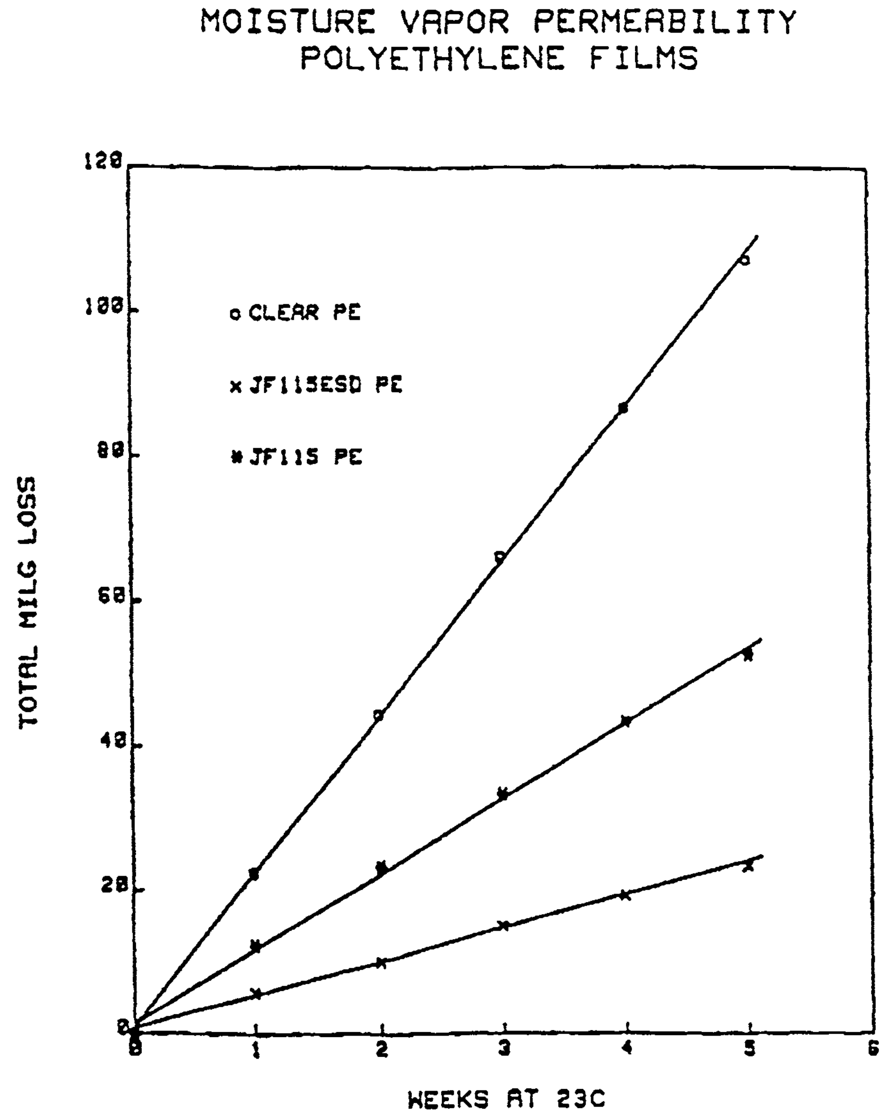


Figure 8. shows superior performance of Corrosion Intercept® compared to Benzotriazole (BTA) and Imidazole (IMDA). Source: Roberts, Hobbins, Graedel, Franey and Kammlott: "Relative Inhibitors of Copper Corrosion by Azoles", Corrosion Intercept Presentation, Bell Labs International *Technical Memo, TM 801517-34,* 1980. Permission by John Franey, co-author and member of Technical Staff, Lucent Bell Labs, Murry Hill, NJ.



AT&T-PROPRIETARY

Figure 9. shows Corrosion Intercept®, seen under JF115 PE code name, the least permeable to moisture vapour among the tested materials. Clear Polyethylene (CLEAR PE) is the most permeable. *Static Intercept®* (seen under JF115ESD PE code name) shows about half of the permeability of a clear polyethylene sheet of the same thickness. Test performed in 1988, on 0.002" thick, that is 2 mil films using the ASTM cup method. Total MILG loss is in grams per hour, per centimeter, per millimeters of mercury. Source: Franey, J.P. and Graedel, T.E.: "A New Electrostatic and Corrosion Protective Polymer" Bell Labs *Technical Memo, TM-11538-901128-06*. JF116. Permission by John Franey, co-author and member of Technical Staff, Lucent Bell Labs, NJ.

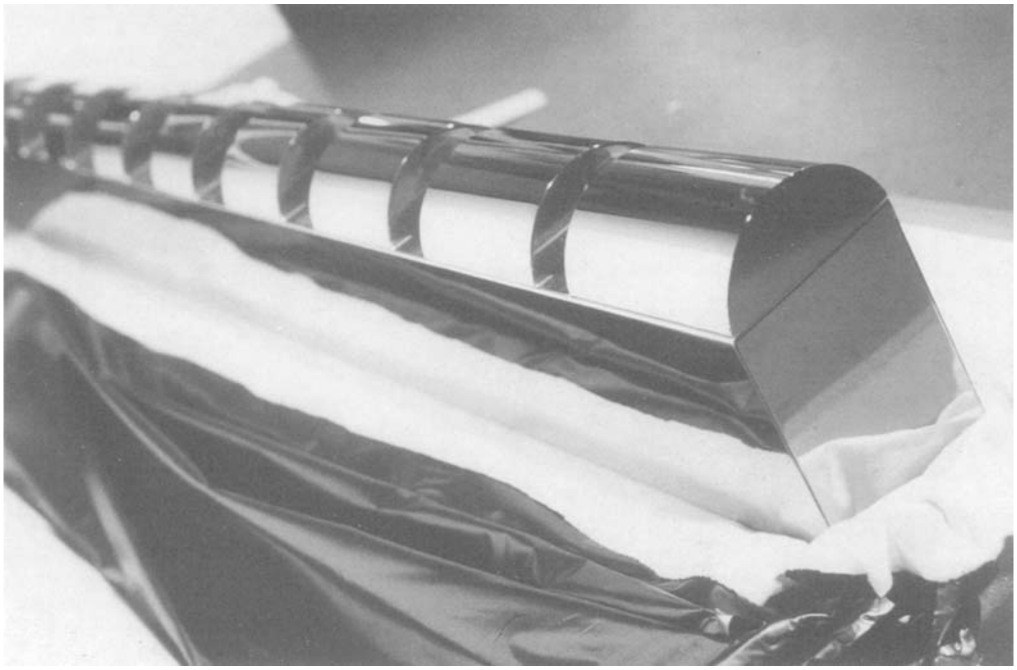


Figure 10. D. Judd: *Untitled 1970*. Copper Progression in pristine condition after six years of storage. Packing system shown: the piece wrapped in pre-washed cotton/polyester fabric, followed by Corrosion Intercept.

Figure 11. D. Judd: *Untitled 1970*. Copper Progression, wrapped in Corrosion Intercept. Packing system continued from Figure 10. Note the overlap of the Corrosion Intercept sheet and the Acrylic Adhesive tape to secure the Intercept in place.

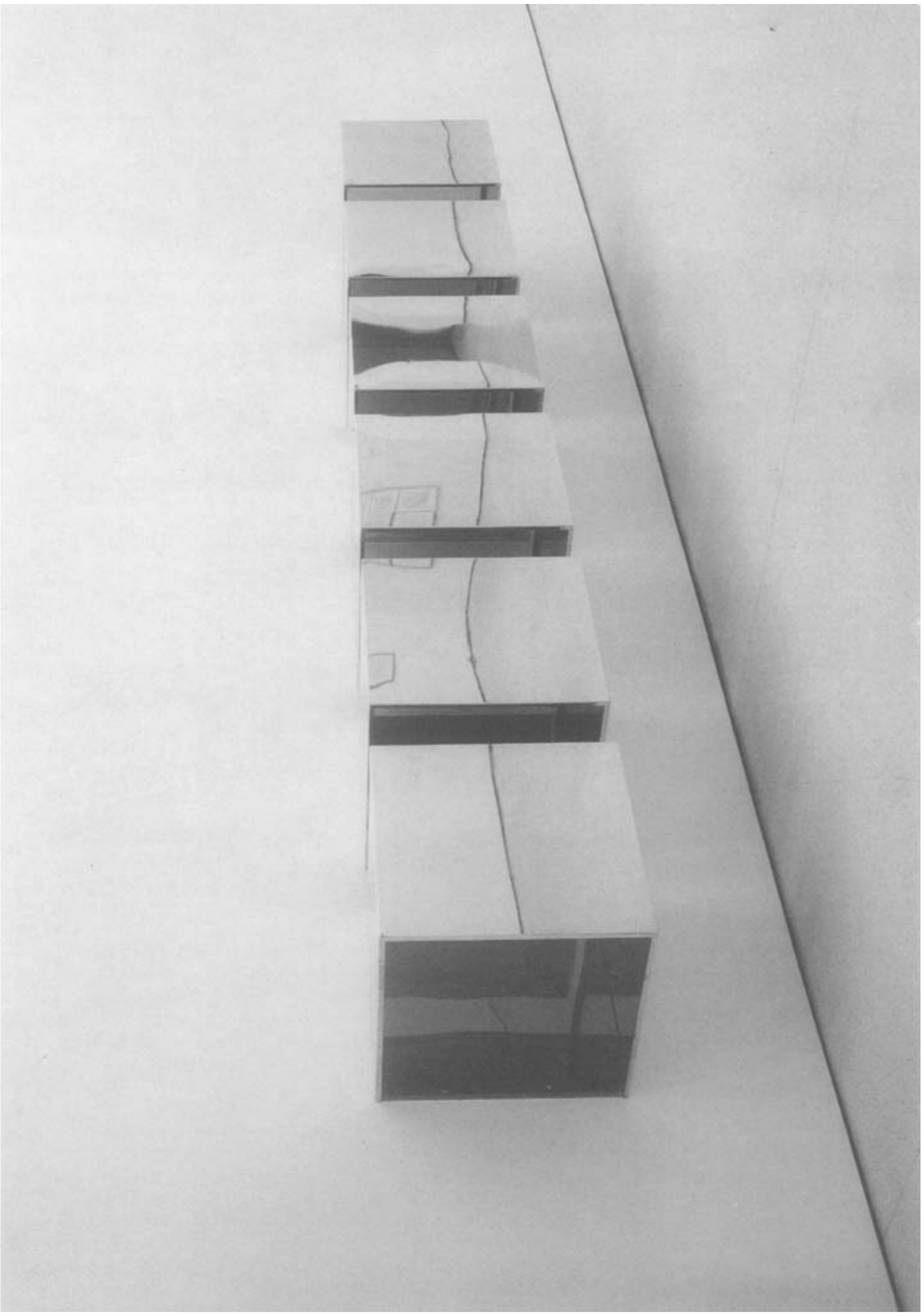


Figure 12. Donald Judd: *Untitled, 1972*. Six Cubes, each 34x34x34 inches. Brass and Plexiglas, Solomon R Guggenheim Museum, New York, Panza Collection, 1991. Photograph by David Heald© The Solomon R. Guggenheim Foundation, New York.

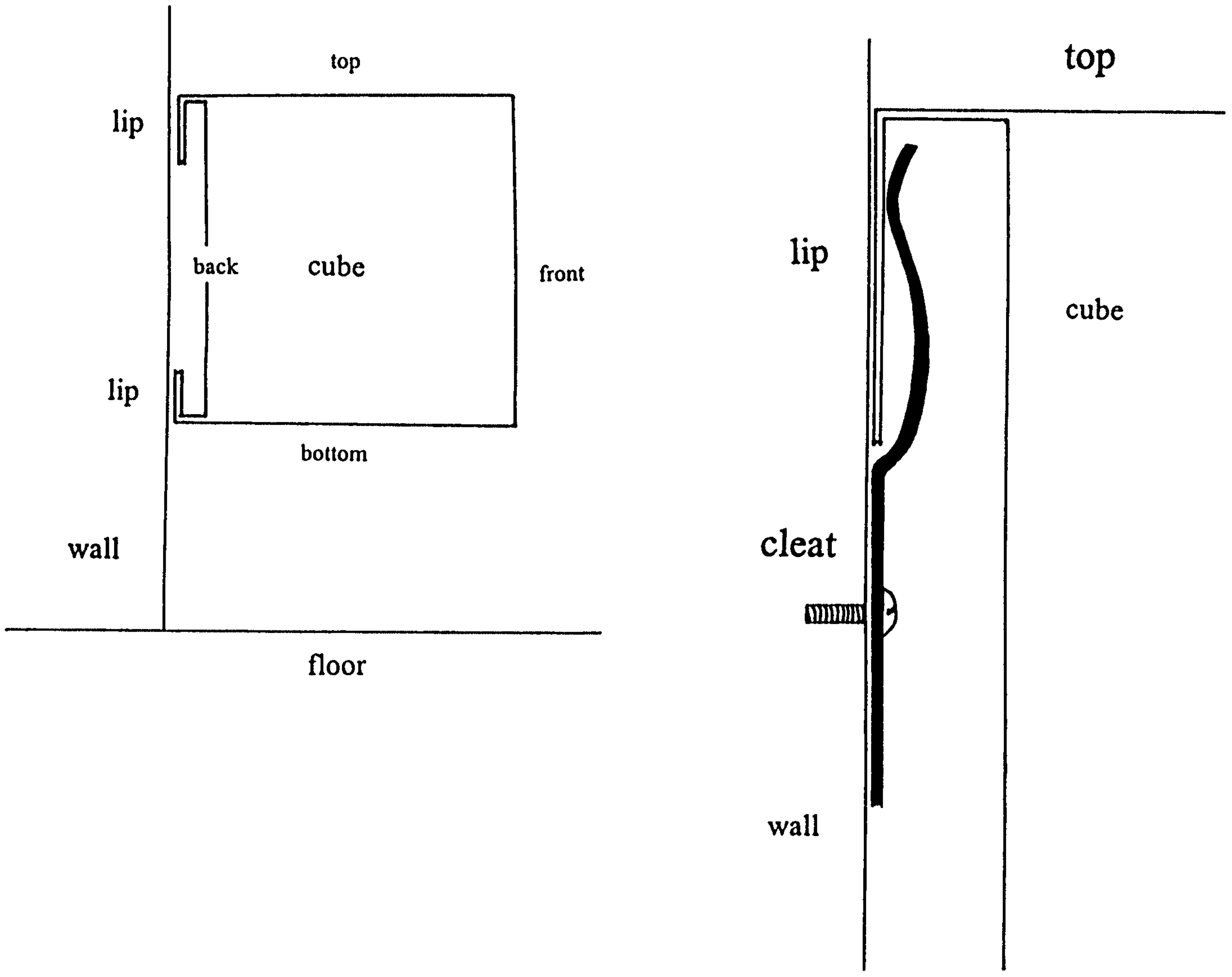


Figure 13. Mechanism of construction and method of hanging.

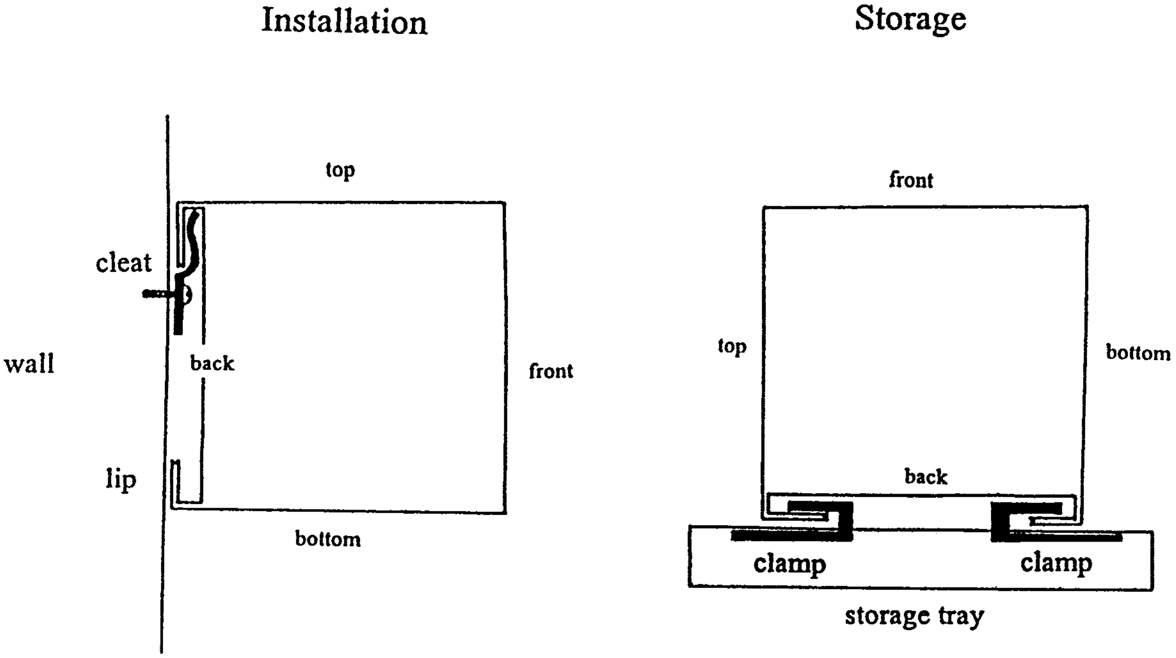


Figure 14. Cross sections of installation and storage mechanisms.

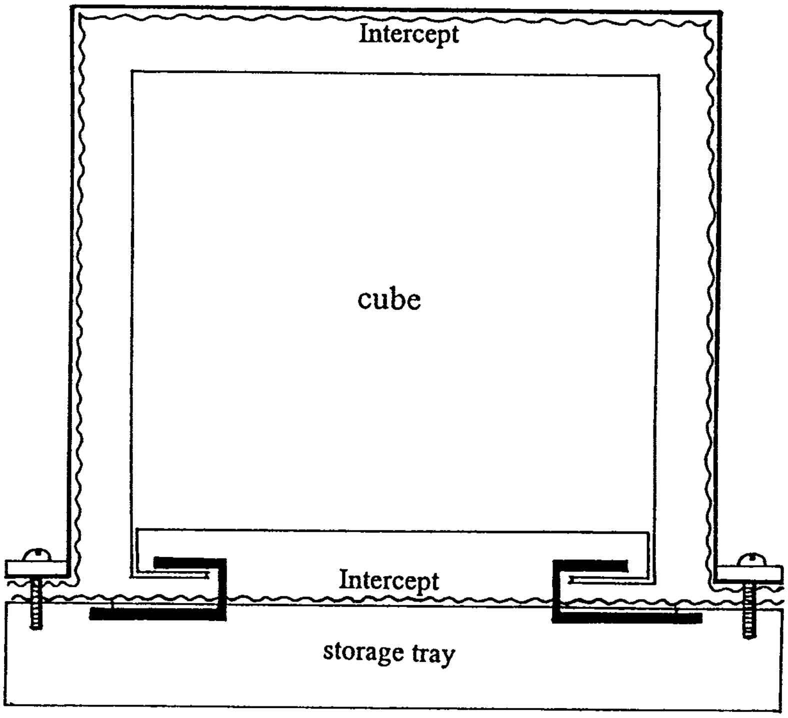


Figure 15. Cross section of Corrosion Intercept® tent on storage tray.

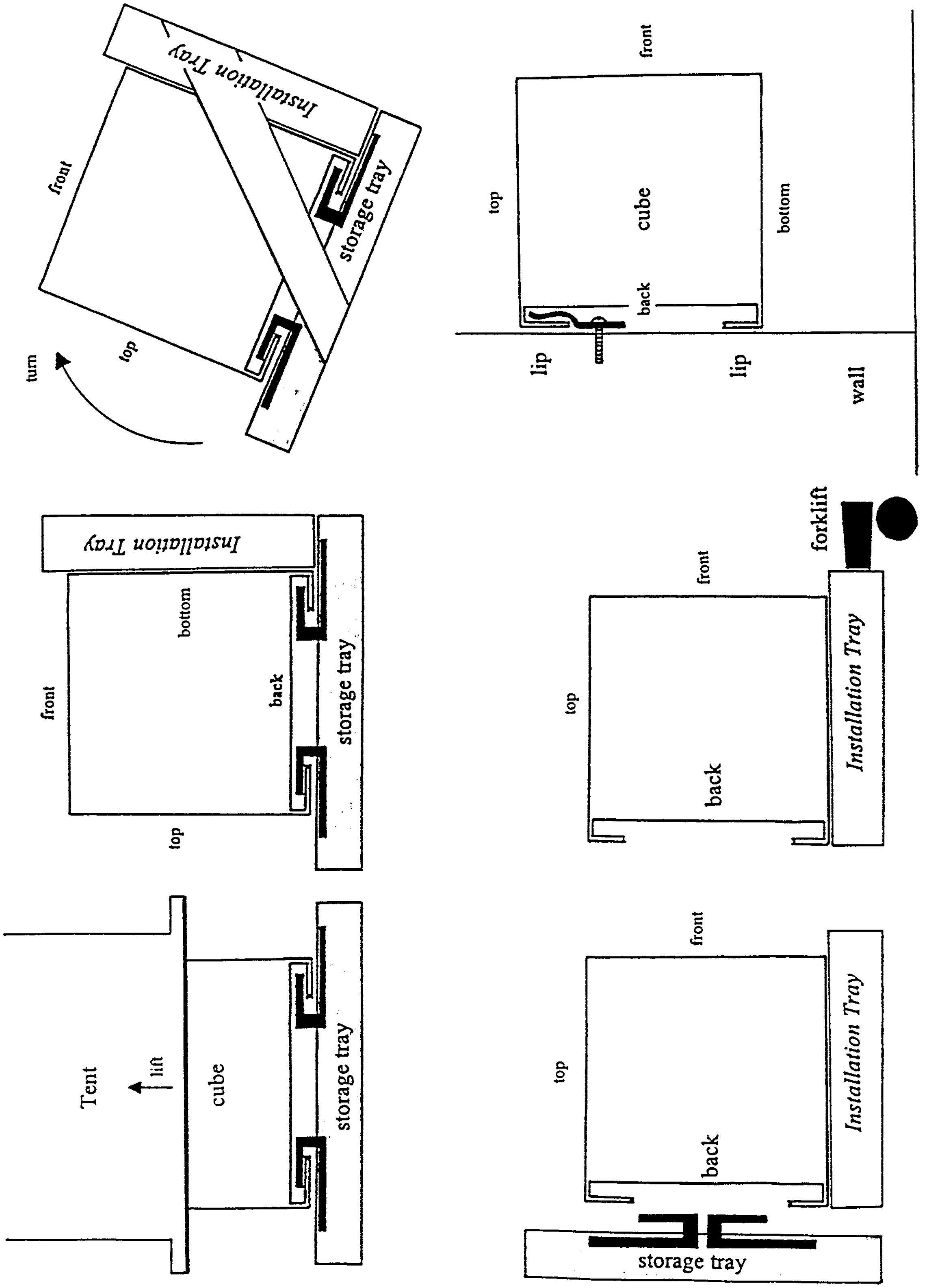


Figure 16. Cross sections showing sequence of object transfer from storage tray to installation.

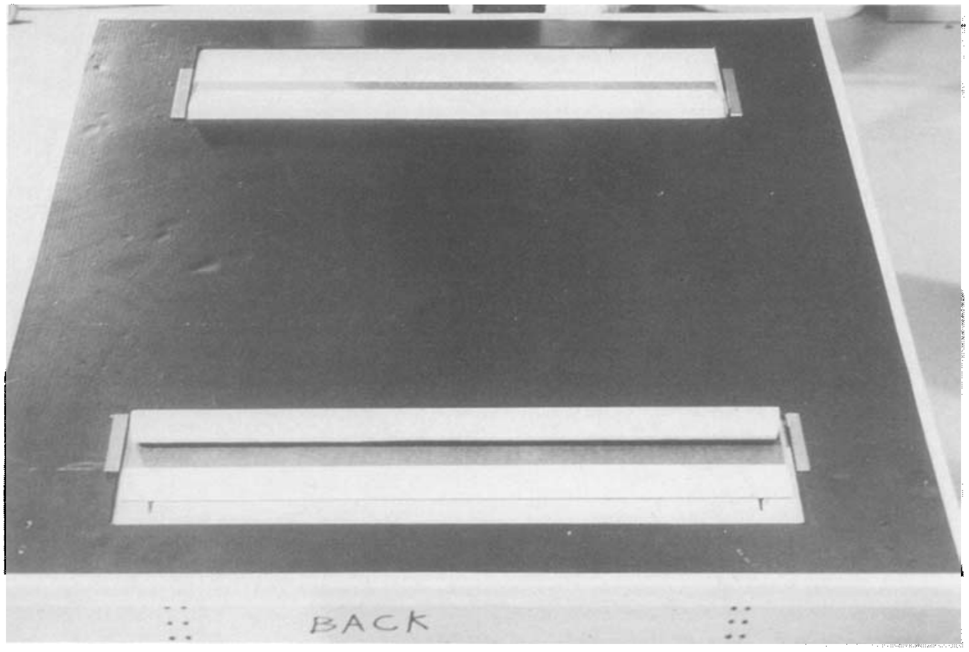


Figure 17. Storage Tray. 46" x46", plywood, covered with acid-free, single ply corrugated cardboard followed by 4 mil Corrosion Intercept and glued with Jade 711 adhesive. Note that the surfaces of the long clamps and the edges of the storage tray are sealed with white Acrylic Adhesive tape. No plywood surface is exposed to the object when the storage tray is in locked position.

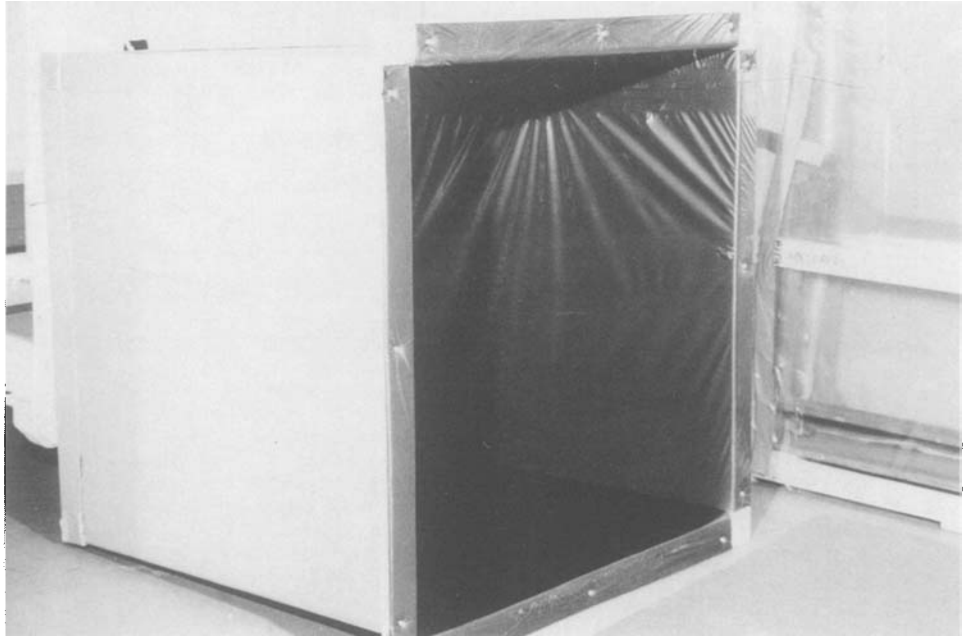


Figure 19. Corrosion Intercept Tent. W46"x D 46" x H40". One layer, acid free, single ply corrugated cardboard glued with Jade 711. The inside of the tent is lined with 3 mil Corrosion Intercept® that folds over the rims. No adhesive was used for lining the inside of the tent. The rim is re-enforced with plywood. Screw holes in the rim (three each side) are for securing the tent to the storage tray.

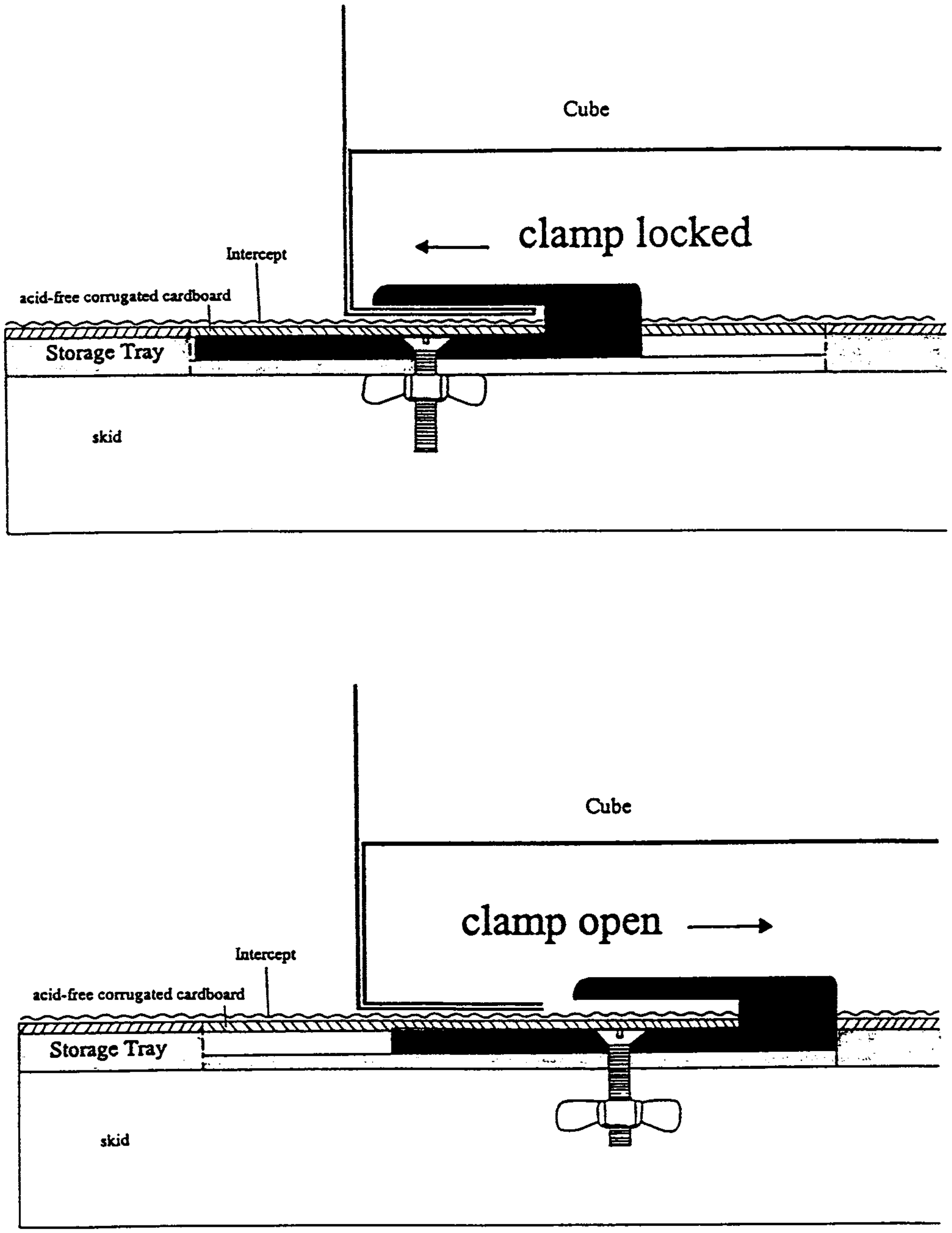


Figure 18. Detailed cross section of clamp mechanism on storage tray.

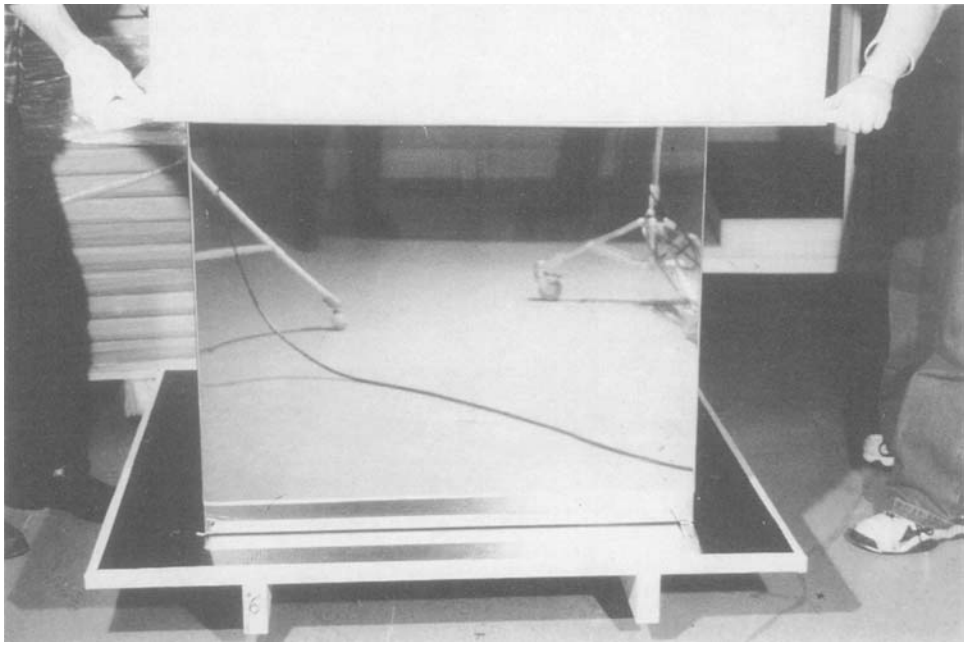


Figure 20. View of the object on the Storage Tray as the Tent is lifted up.

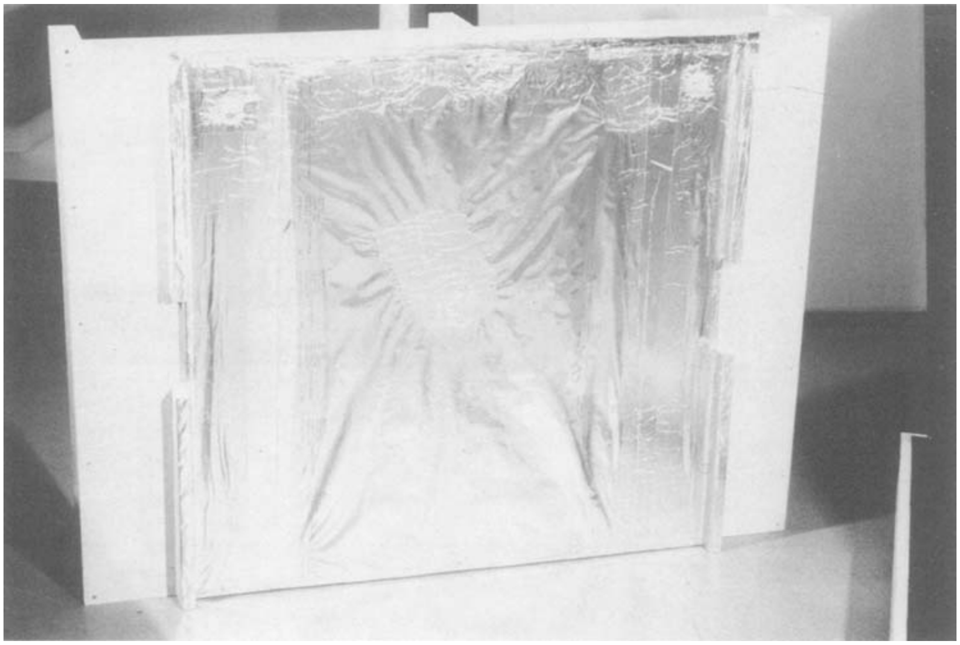


Figure 21. Installation Tray. 46" x 36". Plywood with footprint of the object. The rim around the footprint and the footprint are covered with Marvel-seal, which is heat-sealed. The footprint of the object aligns with the edge of the installation crate (edge seen at the floor).

It is essential to ensure that the clamps are in plane with the top of the storage tray, to allow free adjustments of the clamps while the object is placed on the tray. The top of the storage tray is padded with a layer of acid free corrugated cardboard and covered with a sheet of 4 mil Corrosion Intercept®, glued to the cardboard with Jade 711.

The tent is made of one layer of acid-free, single-ply corrugated cardboard and glued together using Jade 711. The tent allows three inches along the perimeter of the object. The inside of the corrugated cardboard tent is lined with 3 mil Corrosion Intercept that folds over the rims, as seen in Figure 19. No adhesive was used for the inner lining of the tent. The tent is secured to the storage tray with screws along the rims, creating a sealed environment.

For installation, the tent is lifted away, but the object remains clamped to the storage tray (Figure 20). A second tray, the installation tray, is made out of plywood. This tray, shown in Figure 21, must provide for the exact footprint of the bottom of the object, with extra width on the two sides for handling, and skids on the bottom for moving with a forklift. The footprint of the sculpture must be aligned on one side, the side that will be against the wall, with the edge of the installation tray. A small rim may surround the exact footprint of the bottom of the object, which will protect the object from slipping in case the tray is not held perfectly horizontal. Both the footprint and the rim have to be covered to protect the object from being scratched. In this example Marvelseal™ (aluminized polyethylene sheet) was used. Using Marvelseal™ for the installation tray ensures clear distinction between the storage and installation trays for installation crew members not familiar with the system.

The next step is transferring the sculpture from the storage tray onto the installation tray. One must place the installation tray in direct contact with the bottom of the sculpture, that is, the side that will be the bottom of the sculpture when installed (Figure 22) The installation tray must fit perfectly to the edge of the storage tray and allow openings for bolting. Note that the installation tray is usually the depth of the storage tray. This allows for easier alignment when the two trays are bolted together. However, one must make sure that, in the case of a sculpture of repeated units, the depth of the installation tray comfortably fits into the smallest space between the units. The installation tray and the storage tray are bolted together and reinforced by two cross bars on the sides. Then, grabbing by the trays only, the object is rotated 90 degrees (Figure 23). The vertical installation tray rotates to a horizontal position (Figure 24). After the clamps holding the lips of the sculpture to the storage tray are unlocked, all bolts and cross bars are undone and the storage tray removed, the sculpture stands on its installation tray, ready to be picked up and installed on the wall (Figure 25). Note that the backside of the sculpture, which will contact the wall, forms a continuous plane with the very edge of the installation tray for perfect contact with the flat wall. It is worthwhile to point out that, for sculptures of repeated identical units, only one installation tray has to be made, as one unit is installed at a time.

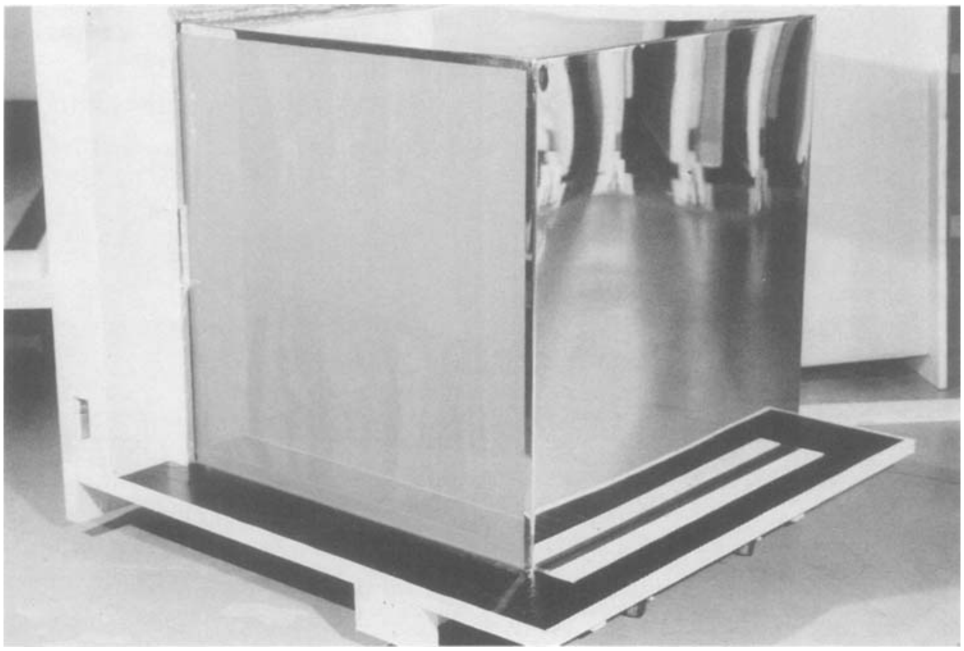


Figure 22. Object clamped to the Storage Tray (seen in horizontal position) and Installation Tray positioned. Note that the installation tray is in contact with the side of the object which will become the bottom when installed. The width of the installation tray is the width of the storage tray.

Figure 23. The two trays bolted and reinforced with cross bars are being rotated 90 degrees.

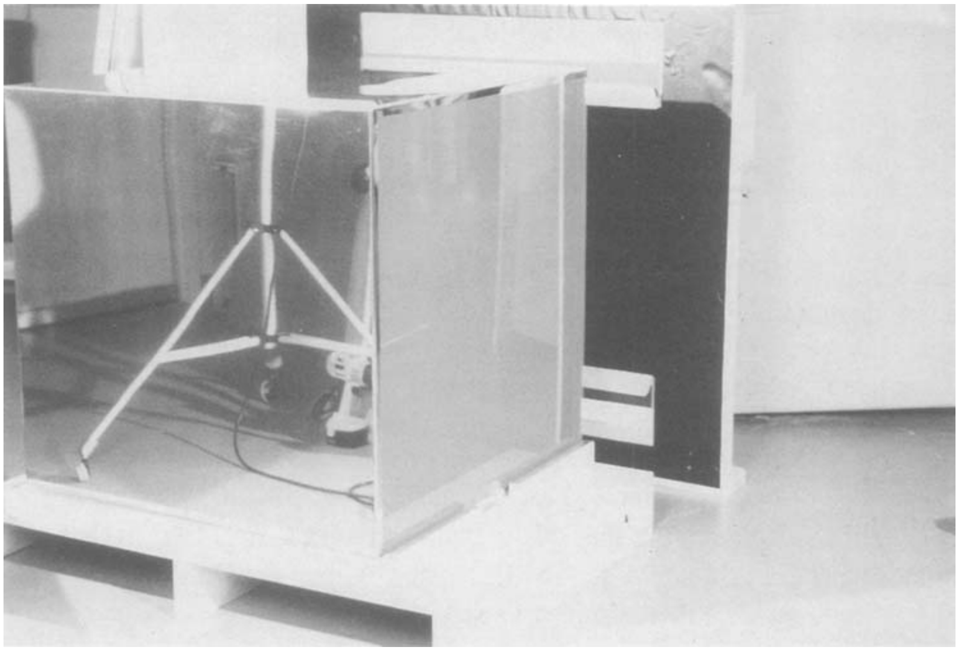


Figure 24. Object standing on the Installation Tray after rotation. The Storage Tray is already unclamped and standing behind the object.

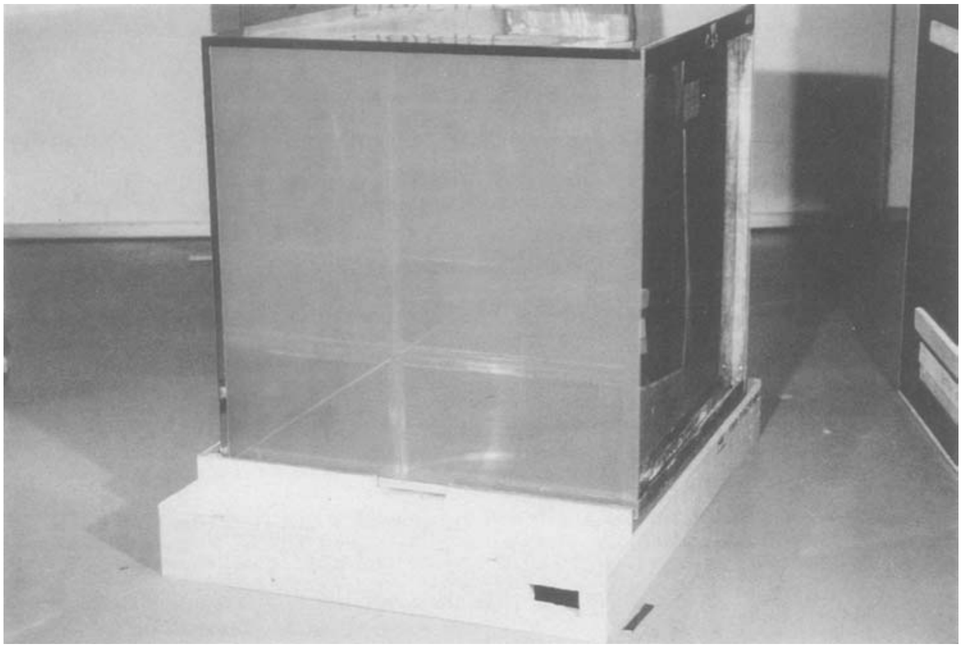


Figure 25. The object standing on the Installation Tray, ready to be installed. Note that the back of the object (the side which will be in contact with the wall) is aligned with the edge of the Installation Tray (seen on the right side). The object can be lifted up by a forklift, accessing the Installation Tray from the front of the object (left side on the image), or can be hand lifted using the cut-out handle.

Conclusion

Various versions of Corrosion Intercept® packing methods have been successfully used and have been continuously monitored since early 1994 at the Solomon R. Guggenheim Museum Conservation Laboratory.

The new Corrosion Intercept®Tent Packing System presented here proved to be the most successful and practical method for the long-term preservation of Donald Judd's highly polished brass and copper sculptures. The system is economical and materials are easy to obtain. Costs are equivalent or lower than standard crate or packing prices. The system is easy to construct, long-lasting and does not need maintenance. It solves frequent storage, handling, installation and transportation problems in one. Sculptures can be successfully preserved and protected long term regardless of their stage of deterioration. Experience at the Guggenheim Museum shows that handling and installation of sculptures using this system is approximately two to three times faster than installations using traditional methods. The Corrosion Intercept®Tent Packing System can be adopted not only to Donald Judd's non-ferrous sculptures, but also to similar modern and contemporary metal sculptures.

Acknowledgements

The development and execution of this project was part of two generous grants received from the Institute of Museum and Library Services and from the Getty Conservation Institute. The author also would like to thank Keith Donaldson at Engineering Materials for his devoted support of this project, John Franey at Lucent Bell Labs for permission of publishing test results on Intercept research, and the Conservation Department and the Art Handling Crew in the TSB building at the Guggenheim Museum for their enthusiastic work and support during the development of this project.

Endnotes

i The black color of a saturated and used *Corrosion Intercept* ® should not be mistaken for the black color of a similar product by the same company, called *Static Intercept*®. Static Intercept was developed for *ferrous* metals. However, it can be used for non-ferrous metals as well.

ii For further information on testing Intercept products see the attached Bibliography or visit the website: *www.staticintercept.com*

iii A decision was made to pre-wash all fabric before use in order to avoid contamination of the metal surface with residues of starch and brighteners applied to the fabric surface by the manufacturer. All fabric was washed in 2% Orvus solution, then repeatedly rinsed in tap water.

100% cotton jersey and a cotton/polyester 50/50% fabric were used for this type of packing system.

iv Jade 711 tested negative for sulfur (test performed by the author) using the *Lead Acetate Test* kindly provided by Jean Tetreault, Canadian Conservation Institute, 1030 Innes Road, Ottawa, ON K1A OC8, Canada. 613-998-3721.

v After the corrugated cardboard/Intercept lined tent was constructed, a new product appeared on the market providing another option for creating the tent. The product's name is *Coroplast*™ *Corrosive Intercept*®. It is 100% Intercept-Polypropylene resin, extruded. It can be heat sealed or stapled to create a box. Coroplast Static Intercept® may be used for the same purpose as well.

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Suppliers

Coroplast™ Corrosive Intercept®: Engineered Materials, Inc. 113 McHenry Road, Suite 179, Buffalo Grove, IL 60089, USA. 847-821-8280, Fax 847-821-8260, E-mail: emipres@AOL.COM

Keepsafe Systems/Object and Textile Conservation Services Ltd. 570 King St. West, Suite 400, Toronto, ON. M5V 1M3 Canada. 1-800-683-4696, 416-703-4696, Fax 416-703-5991. www.interlog.com\~keepsafe

Polyfoam M & G Packaging Corp. 226-10 Jamaica Avenue, Floral Park, New York, NY. 11001, USA. 718-343-0343, Fax 516-488-3181

Volara: Closed-cell polyethylene foam sheet, Foam-Tex Inc. 150 West 22nd Street, New York, NY. 10011-2421, USA. 212-727-1780, or Rogers Foam Corp. 150 East Post Road, Morrisville, Pennsylvania, 19067, 215-295-8720 Fax 215-295-3993

Acrylic Adhesive Tape, Conservation Resources International, L.L.C. 8000-H Forbes Place, Springfield, Virginia, 22151, USA. 1-800-634-6932, Fax 703-321-7730.www.conservationresources.com

Marvelseal: Benchmark , P.O.Box 214, Rosmont, NJ, 08556, USA. 609-397-3731, Fax 609-397-1159.

Dazey Vacuum Seal-a-meal, Household Heat Sealer, Dazey Corporation, One Dazey Circle Industrial Airport, KS 66031, available at Household Ware Stores

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THE EFFECTS OF COMMERCIAL PHOTOGRAPHIC DULLING SPRAYS ON SILVER OBJECTS

David Harvey

Objects conservators often encounter the effects of foreign chemicals and materials that have been applied to the surfaces of objects. These contaminants can range from the use of household cleaners, the residues from floods and fires, and restoration materials. The case study in this paper explores the problem created by the application of a commercial photographic dulling spray on reflective silver surfaces to eliminate glare. The use of dulling sprays on metals and other artistic and historic objects has only been documented anecdotally as a search of the conservation literature contains no mention of them. The use of these dulling sprays seems to be a widespread phenomenon. One only needs to turn the pages of the major auction and exhibition catalogues and magazines to appreciate the scope of this practice by photographers. In this paper we will explore the way that the materials and solvents in the dulling spray can initiate damage to historic silver and the challenges that its removal presents to formulating a successful treatment.

In July, 1997 the Metals & Arms laboratory at Colonial Williamsburg discovered that a Scottish silver Newbattle Kirk Cup made by George Cleghorne (Edinburgh, Scotland, ca. 1644-1646) had been coated with commercial photographic dulling spay by a department of collections volunteer photographer. The photographer had applied the spray, photographed the silver cup, and then wiped the surface with a cloth. The cup was further affected in storage by an HVAC failure during a thunderstorm in which the relative humidity in the storage area spiked to 90% within a 24 hour period.

The surface of the cup had visible white crystalline particulate accretions - especially prominent on the bowl interior. Finger-wipe marks were visible within the accretions. There were also numerous black/gray tarnish spots over all of the surfaces of the cup with the exception of the underside of the foot. When the black tarnish spots were viewed under a low-power binocular microscope they were found to consist of etched tide rings around seams and pores in the silver. This etching mechanism is liquid-based, as evidenced by the tide rings visible around seams and pores where the dulling spray had accumulated. The white particles migrated to the outer edges of the tide rings as the liquid carrier (i.e.. solvents) evaporated. This phenomenon is similar to water-spotting on glass.

The observed mechanism is important for two reasons. First, it is idiosyncratic, and distinct from normal silver sulfide tarnish. Second, it is a vastly more damaging corrosion mechanism because it is an etching phenomenon rather than a film-forming phenomenon (such as normal silver sulfide tarnish). Etching corrodes through the fine silver to the underlying fire-scale leaving a pitted and eroded surface.

Photomicrographs clearly show that the white particulate is highly abrasive - with a new scratch pattern visible. This new damage is evidenced by the fact that it has neither oxidized nor tarnished, and it overlies older scratches and scars on the silver surface which have patina.

In the act of applying the dulling spray and wiping it off, tiny white particles were driven into the micro-interstices of the surface (i.e.., pores, seams, scratches) where they could form localized corrosion cells and etch through the metal. The high relief of the silver surface has been entirely refinished with a new scratch pattern which exposes a vast surface area for cycles of fresh tarnish and corrosion. Metals are especially susectible to corrosion from solid particles as low-pH microenvironments form underneath them, eventually creating a pit on the metal surface.

Testing of a sample with XRD indicated that the white crystalline particles are titanium dioxide (TiO2). It is important to note that silver has a Moh hardness of 2.5; anatase and rutile (the two forms of TiO2) have Mohs hardnesses from 5.5 to 6.5. The particulate material in this dulling spray is at least 220 percent more abrasive than the silver substrate.

A replicant coupon corrosion study conducted in an electrochemical cell of replicated sterling silver indicated that coupons which have been exposed to dulling spray are quantitatively more corroded than coupons which have not been exposed to the dulling spray. It was important to use silver raised from ingot so that the microscopic layers of fire scale and silver were present, since modern silver lacks the oxidation inherent in the traditionally formed sheet metal. This experimental trial proves that the presence of the dulling spray on the surface of the object does cause measurable damage (i.e., etching) and erosion of the original surface.

The tiny opaque particles from the spray appeared as agglomerations of tiny crystals. Upon subsequent study under high power magnification these crystals were found to be approximately 1 micron in size. The crystals were driven into every seam, pore, and scratch in the silver where the carrier solvent had been retained keeping the particles agglomerated. Particles 1 micron in size or less are subject to Van der Wals forces which makes their removal problematic.

Under high magnification the tiny titanium dioxide crystals aggregate and form plate-like layers when sprayed on a microscope slide. This forms micro-cavities which trap liquid and air and only release them slowly - the liquid being retained by capillary action. This observation is important because it explains why the dulling spray particles have a measurable corrosion rate. This also might aid in explaining why the cup suddenly appeared to corrode so quickly - given the relative humidity spike that the cup received while in storage.

The treatment of this 17th century Scottish silver cup became a classic conservation problem. Traditional silver cleaning and polishing techniques would simply exacerbate the situation as any mechanical cleaning would only continue the abrasion of the historic silver cup. The micron sized abrasive crystals had to be released from the silver substrate first and cleared entirely before tarnish removal could be undertaken.

A treatment plan was formulated utilizing a non-ionic surfactant (Pluronic 17R4 made by BASF

Corp.) 3% in ethanol and applying focused ultrasonic energy from a Misonix XL 2007 ultrasonic wand. Any remaining particles and surfactant was cleared by immersion in ethanol and cleaning again with the ultrasonic wand. After the particles were completely released from the surface a more traditional silver treatment utilizing 0.05 gamma alumina in deionized water was carried out. The conservation polish was cleared by immersion in deionized water in a 40 Mz ultrasonic tank. The cup was immediately dried in an industrial hot air dryer using filtered air and then degreased with Stoddard solvent. After drying the cup was lacquered with two coats of Agateen lacquer #27.

Although this problem was successfully dealt with in treatment, irreversible damage to the object did occur, and the investment of time in the lab far outweighed the benefits of time savings in photography. The use of commonplace photographic practices such as utilizing a light pen or diffusion filters could easily curb any problems with object reflectance without adversely affecting the object.

Since this is a problem that can and should be prevented it hoped that the publication and dissemination of this paper will make a contribution to raising the awareness of our colleagues in museums and auction houses who photograph historic and artistic metal objects.

Dedication

This article is dedicated to my great friend and mentor Ann Van Orden, Assistant Professor in Mechanical Engineering at Old Dominion University. Ann shared her expertise in corrosion and her enthusiam for science with me on this project and numerous others. She died of cancer in 1998, before the publication of this article.

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Figure 1. Before treatment view of the underside of the Cleghorne Church Cup. Note the etch spots, especially the "tadpole" shaped spot. Photograph by the author. Courtesy of the the Colonial Williamsburg Foundation.

Figure 2. 20x view of the "tadpole" etched spot on the Cleghorne Church Cup. Note the accumulation of the white particulates in both the seam and at the outer edges of the tide ring. Also note the new scratch pattern visible above the fire scale of the sterling silver surface. Photomicrograph by the author. Courtesy of the Colonial Williamsburg Foundation.

Figure 3. After treatment photograph of the Cleghorne Church Cup. Photograph by the author. Courtesy of the Colonial Williamsburg Foundation.

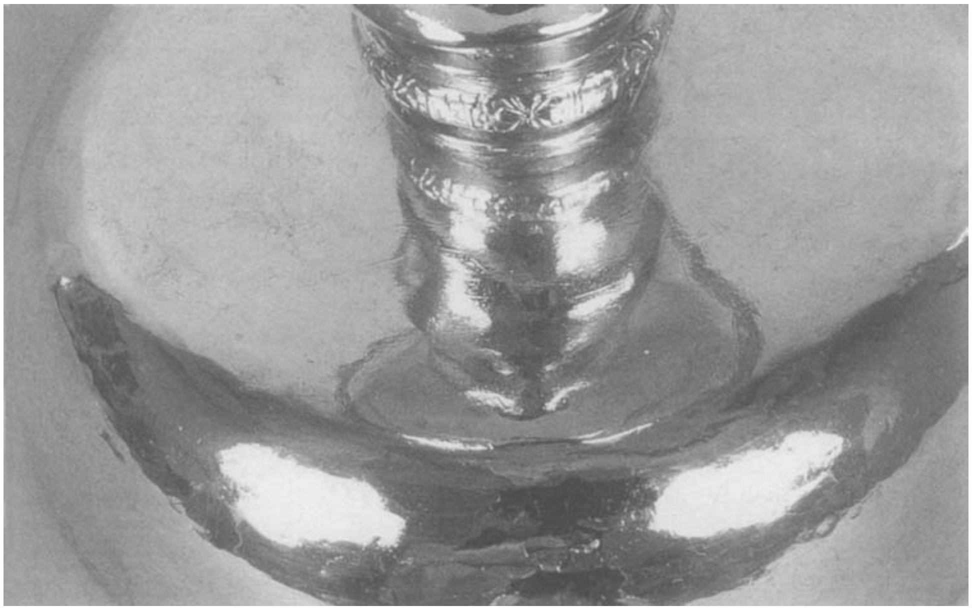

Figure 4. After treatment detail of the Cleghorne Church Cup. Compare to the before treatment view in Figure 1. Photograph by the author. Courtesy of the Colonial Williamsburg Foundation.

EVALUATION OF THREE PROTECTIVE COATINGS FOR INDOOR SILVER ARTIFACTS

Chandra L. Reedy, Richard A. Corbett, Deborah L. Long, Robert E. Tatnall, and Bradley D. Krantz

Abstract

Three coatings commonly used for protection of silver artifacts housed indoors (Agateen, Paraloid B-72, and Paraloid B-48N) were tested to rank their performance. Protocols were developed to be relevant to conservation practice, while also incorporating industry testing techniques. A variety of test specimens were used to check for effects of complex geometry and sterling versus fine silver, and to measure changes occurring on the silver beneath the coatings as well as changes of the coatings themselves. Accelerated aging included exposure to fluctuating temperature and relative humidity, and to a variety of common pollutants (hydrogen sulfide, sulfur dioxide, ozone, formaldehyde, and acetic acid). Both visual ranking and quantitative tests were used; data were analyzed for statistical significance by one-way and two-way analysis of variance. Our results show that Agateen protects silver from hydrogen sulfide, even after great environmental stress (i.e., accelerated aging), whereas the two acrylic coatings offer no protection. All three coatings begin to crack and peel slightly after accelerated aging. For the bent specimens with more complex geometry, brushing provides better protection, as otherwise the coatings tend to peel away from edges. For protection against hydrogen sulfide, spraying was sometimes more effective, perhaps because it may result in a slightly thicker and more even coating. Our findings correspond with our field observations and the reported experiences of many conservators. Conservators are sometimes reluctant to use Agateen due to problems with other cellulose nitrate lacquers and to the severe degradation any cellulose nitrate can endure if exposed to very high temperatures or to direct sunlight. However, given the preferred application and appearance qualities of Agateen, our results support its continued use for coating of silver for indoor environments.

1. Introduction

Most silver artifacts in the collections of museums and historic buildings are coated to protect against the easily-developed tarnish that detracts from the appearance of objects, obscures important details, and creates time-intensive cleaning and polishing maintenance work. The choice of coating is crucial, since coating failure can result in even more destruction to the object than occurs with no coating at all. A failed coating may require significant time for removal, cleaning, and recoating. However, the repertoire of coatings currently in use in the conservation field is rather limited. Only limited test reports of those coatings exist in the literature and the use of some is controversial, with conservators reporting conflicting experiences with their use.

Reviewing the limited number of studies of coatings for metal artifacts housed indoors, the one most frequently cited by conservators was published about 25 years ago (De Witte 1973). In this study, thirteen coatings were tested. The tests were not actually performed on silver or copper specimens, but rather on tin-plated iron. The testing protocol has been criticized because of the use of an extremely high temperature (90°C). Such an extreme temperature is not realistic for most conservation applications and, most importantly, is known to thermally decompose some of the coatings tested, especially the cellulose nitrates (Selwitz 1988). Thus, such a protocol makes for an unrealistic test.

Most published test results for coatings within the conservation field have focused primarily upon those used for outdoor sculpture. Tests typically involve exposure to "outdoor" environments such as sunlight, acid rain, and normal outdoor pollutant types and levels, and are usually performed on coatings applied to bronze, steel, zinc, lead, or iron substrates. Most of these tests include coatings and components other than those used for indoor silver artifacts such as paints, waxes, Incralac, benzotriazole and other corrosion inhibitors.

Here we focus on three coatings currently used by conservators for indoor silver protection: Agateen, a cellulose nitrate; and two acrylic polymers, Paraloid B-72 and Paraloid B-48N. Agateen has a long history of use as a silver coating (Heller 1983). However, some conservators fear deterioration problems with it, and have ceased to use it. Yet others still use it on a regular basis because of its advantageous working properties, and have not reported experiencing deterioration problems. The stability and reversibility of Paraloid B-72 are well-studied (Feller and Curran 1975; Feller 1984). Although these properties are somewhat affected by age and oxidation, B-72 is considered an excellent material for many conservation applications (Feller, Stolow and Jones 1985; Koob 1986). Most of the testing of B-72, however, has been for the purpose of assessing its use as a varnish for paintings or as a consolidant or adhesive for ceramics and glass. Its strong performance in those tests has lead to its selection as a silver coating. Unfortunately, tests of other applications cannot accurately predict performance as a metal coating since the substrate and demands on the coating are so different, and the percent solids generally differ. These factors can affect coating properties; and, of course, with other uses, corrosion development is not an issue. Paraloid B-48N is marketed as a coating for use on bare metal, but some conservators have avoided it because of alleged problems with yellowing and discoloration. Clearly, all three of these coatings currently in use by conservators need in-depth, objective tests for their performance when used on silver artifacts housed in an indoor environment.

The testing protocols developed in this study were aimed at maintaining relevance to actual conservation situations, while also incorporating new industrial testing techniques. Accelerated test methods were used to compare the relative merits of the three coatings in their ability to protect silver substrates against corrosive pollutants typically found in museums and historic houses. Since objects in museums and historic houses are not normally exposed to high levels of UV light, but rather are more likely to be exposed to elevated temperatures and high humidity, these tests combined the latter destructive factors, thus avoiding the extreme temperature that would decompose Agateen. It has long been noted in the literature than common environmental pollutants which are off-gassing products in storage or display case materials may affect coated metals (Oddy 1973; Padfield, Erhardt and Hopwood 1982; Hackney 1984; Donovan 1986; Hatchfield and Carpenter 1987; Hisham and Grosjean 1989; Nazaroff and Cass 1989; Druzik et al 1990; Grzywacz and Stulik 1991; Grzywacs and Tennent 1994; and Thickett, Bradley and Lee 1998). The tests therefore included exposure to common indoor pollutants such as hydrogen sulfide, sulfur dioxide, ozone, formaldehyde and acetic acid.

Although silver is very resistant to corrosion from most sources, it does react readily with sulfur in a reduced state of oxidation, as found in hydrogen sulfide, to form silver sulfide, the principal tarnish product found on silver. As has been reported in the conservation literature (Sease et al 1997), high levels (i.e., a few parts per million) of this tarnishing pollutant can develop inside display cases, off-gassed not only from case materials, but also from artifacts that may be housed with silver. Tightly sealed storerooms can also build up high levels of sulfur pollutants. To exacerbate the problem, high levels are not required to initiate tarnish; hydrogen sulfide can tarnish silver at concentrations as low as 10 parts per billion (Pope, Gibbens, and Moss 1968). Carbonyl sulfide, a dangerous tarnishing agent for silver, can also be released from wool and other keratinaceous materials found with artifacts, or materials used in construction of exhibit cases or storage units (Brimblecombe, Shooter, and Kaur 1992). Although reduced sulfur tends to be increased by indoor-generated pollutants, sulfur dioxide levels may be the result of entrance of outdoor-generated automobile pollution (Richey 1982). It is possible that sulfur dioxide attacks silver, along with hydrogen sulfide (Addicks 1940; Thomson 1965).

Since application error and difficulty are acknowledged causes of failure for silver coatings, a variety of shapes and surfaces were used in our testing program. Rather than using flat test specimens, bent L-shaped and engraved surfaces were used to mimic the types of surfaces conservators would normally need to coat and protect from tarnish. Both sterling silver and unalloyed silver were used. Coatings were either sprayed or brushed onto the test specimens. To provide a quantitative measure of corrosion (tarnishing) which might occur under either a sound or a failed coating, flat-surface electrical resistance atmospheric corrosion sensors made of silver were utilized. The results were also assessed visually, but incorporated such experimental design features as randomization, replication, controls, blind assessments, multiple assessors, and statistical tests. To quantify visual changes in the coatings themselves as opposed to changes in the silver substrates as tarnish developed, color changes of coatings were measured on glass tubes with a spectrophotometer after accelerated aging. Finally, information was gathered on actual coated objects in collections to compare the results with conservator's experiences, and to see how (and if) certain coatings have failed during service.

2. Methods

2.1 Coatings

The three coatings tested -- Agateen, Paraloid B-72, and Paraloid B-48N, were selected because they are currently in use as coatings for silver artifacts. They were prepared using protocols that mimic actual conservation applications.

2.1.1 Agateen

Agateen is a cellulose nitrate coating available as a proprietary mixed solvent manufactured by Agate Manufacturing Company. For use as a metal coating it is further diluted with lacquer thinner to about 10-15% solids by weight. While the long-term stability of cellulose lacquers has been questioned, many conservators select it for its good working properties. For example, Heller (1983) prefers it over acrylic polymers as a silver coating because he feels it has superior spray application properties, tends not to run, levels well, has a slower evaporating solvent, and produces a satisfactory surface quality in which the coating is essentially invisible to viewers of the artifact. We used Agateen Lacquer No. 27, diluted with 3 parts Agateen Lacquer Thinner No. 1, the concentration advised by the manufacturer.

2.1.1 Paraloid B-72

Paraloid B-72, manufactured by Röhm and Haas, is a copolymer of ethyl methacrylate and methyl acrylate. It is supplied as pellets and is prepared as a solvent solution; it is soluble in acetone, toluene, xylene, and lacquer thinners (de Witte et al 1978; Koob 1986; Röhm and Haas 1990). Based on recent research regarding variations in coating properties for an acrylic polymer dissolved in various solvents (Hansen et al 1991; Hansen 1994) xylene was chosen as the solvent. Paraloid B-72 has undergone much testing in the conservation field (Feller and Curran 1975; Feller 1981; Koob 1986), primarily for use as a varnish, adhesive, and consolidant. It has been found to be a very stable material, resistant to oxidation, light, hydrolysis and heat, maintaining transparency and reversibility for extended periods of artificial aging.

The B-72 was prepared as a 10% wt/vol in a 95% xylene and 5% butyl cellosolve solution. The butyl cellosolve (ethylene glycol monoethylene) is sometimes added by conservators as a leveling agent to reproduce the prized leveling quality of Agateen; otherwise it is difficult to apply this coating without bumps appearing on the surface.

2.1.3 Paraloid B-48N

Paraloid B-48N, also manufactured by Röhm and Haas, is a copolymer of methyl methacrylate and butyl acrylate. It was designed primarily for clear and pigmented coatings for metals, and is listed as having good adhesion, durability, toughness, flexibility, and weathering characteristics. It too is generally prepared as a solvent solution of dry powder pellets (Röhm and Haas 1990). Again xylene was chosen as the solvent, for fast evaporation (Röhm and Haas recommends either toluene or xylene).

The Canadian Conservation Institute (Down et al 1992) undertook natural aging of both Paraloid B-72 and B-48N in light and dark environments for a period of three to five years. In discoloration tests carried out for five years in dark conditions, B-48N exhibited less yellowing than did B-72. However, Feller (1981) found that acrylics containing butyl and amyl esters have a greater tendency to crosslink, so it was unclear which of the two acrylic coatings might be expected to perform the best. As with the B-72, B-48N was prepared as a 10% wt/vol solution, also in a 95% xylene and 5% butyl cellosolve solution.

2.2 Coating Application

Application protocols were chosen to reproduce the application methods commonly used by conservators. Most silver coatings are either brushed or sprayed on (Wharton 1997). Thus each coating was applied by both methods. Brushing was accomplished with a soft-bristled artist's brush (Figure 1). Spraying was performed using a Devilbis spray gun at 20 psi (Figure 2).

2.3 Substrates and Replicates

The form of test specimens was carefully considered to maintain as much relevance as possible to actual conservation situations. There was a desire to conduct a variety of tests, including assessment of visual changes, quantitative measurement of corrosion, and evaluation of changes occurring with the coatings themselves, in addition to corrosion formation. Therefore a variety of substrates were employed: bent specimens of sterling silver, fine silver coins, electrical resistance atmospheric corrosion sensors made of thin silver films, and glass tubes. The assembled test specimens represent a wide range of surfaces and shapes typically encountered with historic silver objects. A sufficient number of replicates for each substrate was included to assure accurate assessment of within- and between-group variation.

All test specimens (bent, coins, sensors and tubes) were marked with identifying numbers. Each specimen was then randomly assigned to a coating treatment using a random number table. This also allowed the specimens to be blindly evaluated as to which coating had been applied.

2.3.1 Bent Test Specimens

Some deterioration effects of coatings on collections objects are often more noticeable on inside or outside edges, and would not appear on the flat test specimens more commonly used in coatings performance tests. It has been noted in the corrosion literature (Carter 1982) that flat test specimens, although advantageous because of ease of coating application in a uniform manner and ease of assessment, are disadvantageous. One of the disadvantages cited is that coatings vary in thickness with the geometry of an irregularly shaped surface. On artifacts, there can be liquid run-off from edges and retention in recesses. With sprayed coatings thin areas can also result from shielding due to complexities of a shape. There may be differing degrees of work-hardening produced during finishing by varying amounts of polishing depending upon geometry, which may influence service performance of a coating. And, there may be unevenness of exposure to the corrosive environment with recessed areas retaining greater amounts of corrodent for longer periods, while the corrodent runs off more readily from sharply angled areas. Test specimens that more closely match the actual types of objects that will be coated in conservation practice are therefore preferable. To ensure that any edge effects or other variability due to coating application on complex artifacts would be detected, bent, L-shaped sterling silver specimens (Figure 3) instead of flat coupons were designed. These were 0.8 mm thick, and 1 square cm per side.

For each experiment, ten bent specimens were coated with each of the three coatings, for a total of 30. Of the ten for each coating, five were brushed and five were sprayed. Four specimens for each coating (two brushed and two sprayed) were left unexposed as controls, housed for the duration of the experiments in a desiccator. Two bent specimens were left uncoated, and were exposed to the same test conditions as the coated objects. These served as controls for the degree of tarnish that could be expected if no coating treatment were applied.

2.3.2 Coins

To detect any problems that might appear on flat surfaces with shallow design engravings, we also included silver coins in all tests. This also provided us with comparative tests on sterling silver (the bent specimens) as well as on silver unalloyed with copper (the coins, 99.95% silver).

For each experiment, four coins were coated with each of the three coatings (two by brushing and two by spraying), for a total of 12 test coins. Two additional coated coins were housed in the desiccator during the experiments, to serve as controls for untarnished initial appearance. Two uncoated coins were also exposed to the accelerated aging environment, to represent the maximum degree of tarnish that could be expected with no treatment.

2.3.3 Electrical Resistance Atmospheric Corrosion Sensors

To provide a quantitative measure of corrosion (tarnishing) which might occur under either a sound or a failed coating, flat-surfaced electrical resistance atmospheric corrosion sensors made of fine silver were utilized (Figure 4). Thin-film electrical resistance corrosion sensors were originally developed to evaluate the effectiveness of vapor corrosion inhibitors (Moore and Miksic 1995). The sensor consists of a thin metal film in serpentine pattern, with two electrical taps at each end and one at the center. It provides a corrosion measurement surface and a reference element coated with an insulating material. Changes in the ratio between the electrical resistance of the measurement element and the reference element of the sensor are related to corrosion (metal loss). These changes in metal loss, as a function of time, are related to a corrosion rate. The sensors are designed to measure metal loss of as little as 2.5 angstroms (Å), and are repeatable to plus/minus one angstrom; thus they can measure even very short-term changes in corrosion levels.

The electrical resistance sensors were used to evaluate each coating's ability to protect the substrate in our harsh environment, whether or not the coating remained intact. Resistance of these foil sensors is measured with a sensitive electrical bridge circuit. The data evaluated the degree of protection, even at or below the threshold of visual detection of tarnishing. Weight loss measurements of metal specimens cannot replicate this precision because the corrosion product (tarnish) film weighs more than the metal oxidized in the process, and removal of such films invariably involves the removal of some sound metal as well.

The sensors were brush coated with the same three coatings as were used on the test specimens (spraying would have provided less control in covering the area of the corrosion measurement surface). For each of three experiments, we used four sensors with each of the three coating materials, for a total of twelve sensors per experiment (two more were left uncoated for comparison). These were exposed along with the other test specimens, and resistance readings taken periodically to ascertain any metal corrosion which may have occurred. The advantage of such sensors is that corrosion can be measured under coatings without disturbing the coatings; it is well known (Carter 1982) that damage to a metal substrate can easily occur without the development of visual corrosion products.

2.3.4 Glass Tubes

For each experiment, four glass tubes were coated with each of the coatings under study. Two for each coating served as controls, and two underwent the same accelerated aging as did the test specimens. The purpose of these glass tubes was to serve as a measure of the deterioration of the coating itself under accelerated aging, without regard for the development of corrosion on a silver substrate. These tubes were to be used for spectrophotometer readings to evaluate color change in the coatings as a result of accelerated aging-induced deterioration. Since applying the coatings to these tubes by spraying or brushing was quite difficult, they were instead dipped in each coating.

2.4 Accelerated Aging Environments

Accelerated aging was performed in simple chambers that could be reproduced in any conservation laboratory (Figure 5). Two chambers were used, one for a wet environment and one for a dry environment; a movable sample holder was constructed so samples could easily be rotated between the two chambers minimizing the handling. Each of the two chambers was constructed using a sealed 20-gallon glass aquarium, set into an insulated plywood box. The removable sample holder was built of Plexiglas; all samples were hung or set into place on this holder, and moved at the appropriate periods from the wet environment chamber to the drier one.

In the wet environment chamber, conditions were maintained at 50° C and 100% RH. A shallow pan of water provided the RH; and heat was introduced with a hot air gun (hair dryer) set into a hole cut into the plywood box (Figure 6). The second chamber was maintained at typical room temperature and RH conditions. Room conditions were not strictly controlled, but were constantly measured (with RH between 50-60% and temperature between 20-21° C).

Our accelerated aging protocols were designed to mimic, as much as is possible, the environmental factors to which silver objects in museums and historic houses are likely to be exposed. In the indoor environment, objects are not normally exposed to high levels of UV light, but may be exposed to elevated temperatures and high humidity; thus our test combines these latter destructive factors but does not include elevated UV exposure. Since it is known that common environmental pollutants and off-gassing products in storage or display case materials can affect coatings, our tests therefore include exposure to common indoor pollutants such as hydrogen sulfide, sulfur dioxide, ozone, formaldehyde and acetic acid.

Conservators have hypothesized that there is a synergistic effect between a mixture of pollutants, such as might be typically found in a storage or exhibition environment, and fluctuating temperature and humidity. Our accelerated tests, therefore, expose specimens to a "cocktail" of volatile pollutants, as well as to fluctuating temperature and relative humidity that may cause stress on the coatings.

The following pollutants were produced and introduced into the first test chamber with elevated temperature and RH:

(1) H_2S, produced with 1% Na_2S, using 1 gram in 300 mL water with pH adjusted to 7.0; the entire solution was placed in a 500 mL beaker inside the test chamber.

(2) SO_2, produced using 0.01 gram of $NaHSO_3$ plus 10 drops of 3% H_2SO_4 in a small weighing boat inside the test chamber.

The following pollutants were introduced in the second, dry test chamber, with room temperature conditions:

(3) Ozone was produced by running an ozone generator at the lowest output for 3 minutes at about 10 ppm into the test chamber, producing an ozone level of about 1 ppm (O_3 will decompose to O_2 in the test chamber). Ozone can have a direct oxidative effect on coatings, so does not need the high humidity to cause deterioration.

(4) Acetic acid, introduced with 1 mL of 10% acetic acid dispensed into filter paper laying in the bottom of the test chamber.

(5) Formaldehyde, introduced as 1 mL of 10% formaldehyde dispensed onto filter paper laying in the bottom of the test chamber.

The level of pollutants present in the atmosphere inside the chambers were monitored using Dräger diffusion tubes. Minimum detection limits include 1.3 ppm for hydrogen sulfide, 0.63 ppm for sulfur dioxide, 0.5 ppm for ozone, 1.3 ppm for acetic acid, and 0.04 ppm for formaldehyde.

The order of placement of test specimens within the chambers was randomized, so that if there were any pockets of high or low concentration of pollutants, temperature, or RH, no single coating would be unilaterally affected. This randomization was achieved by placing specimens in numerical order, since the numbered coupons had been randomized during coating treatment.

2.5 Methods of Evaluation

Coating performance was assessed both visually and quantitatively. Statistical tests were used to help evaluate both methods of assessment.

2.5.1 Visual Assessment

For bent specimens and coins, the objects were removed from the test chamber holder in the same randomized order in which they had been placed. Using the uncoated controls as one end of the scale (maximum tarnish) and the coated specimens kept in a desiccator as the other end of the scale (original appearance of freshly coated objects), the specimens were ranked from best to worst. Biased judging was avoided by the use of numerical codings, so that judges were unaware of which coating had been applied to each specimen. For the first two experiments, multiple independent judges ranked all specimens. Since there proved to be no significant difference between their rankings, the multiple rankings were deemed unnecessary and were dropped for the final experiment.

One of the factors considered here are presence of visible corrosion (tarnishing) under the coatings, usually appearing as localized or an overall black film; as well as changes in the coating itself which may include cracking, peeling, blistering, hazing, or discoloring. Both coating deterioration and silver tarnish may be present. Aesthetic parameters are considered as important as functional parameters, since cultural artifacts are intended to be viewed by the public, and any change in appearance that detracts from seeing the object as was intended by those who originally made it is unacceptable.

Analysis of these data were conducted using a standard statistical test designed for two-factorial experiments (coating and application method), a two-way analysis of variance (ANOVA) (Dixon 1988; Reedy and Reedy 1994). The null hypothesis is that all group means are equal. A test statistic is calculated using the observed divided by the expected variance of the group means, as computed from group number, sizes, and variances. The *p*-value is the probability of getting a test statistic as extreme as that observed, and tells whether or not the null hypothesis is supported. With a two-way ANOVA, the interaction effects could also be statistically evaluated (e.g., whether the effect of application method varies significantly from one coating to another).

2.5.2 Quantitative Assessment

The electrical resistance atmospheric corrosion sensors provided a quantitative measure of angstroms of metal loss, or loss of conductivity as metal was converted to corrosion products. Data interpretation for the sensor data was done by analysis of variance using the same BMDP program. Since only one application method was present, there was no need to check for any interaction effects, and thus a one-way ANOVA was used.

The coated glass tubes were assessed using a spectrophotometer to measure the change that occurred during accelerated aging exposure, measuring different wavelengths: 470 nm (blue), 580 nm (yellow) and 650 nm (red). The instrument was calibrated initially by setting the light transmission through an uncoated glass tube at 580 nm to "100". A medium sensitivity setting was used throughout.

2.5.3 Reversibility

In conservation practice, reversibility of any treatment is considered extremely important. The Code of Ethics of the American Institute for Conservation stresses this factor, and urges conservators to avoid using any materials that cannot be removed in the future if that becomes necessary (AIC 1998). In the case of protective coatings for tarnishable metals, this is a significant concern because experience has shown that even the best coatings eventually will have to be removed and replaced. Any coating which cannot be removed without risking damage to the substrate is, therefore, clearly unacceptable.

To evaluate comparative reversibility, each coating was tested with both acetone and xylene. A brief swabbing with cotton or dipping in these respective solvents needs to completely remove the coatings in a relatively short period of time, since one would never want to expose an artifact to a strong solvent for extended periods. Therefore, the specimens were first swabbed with solvent to observe changes in solubility which may have occurred as a result of the artificial aging. They were then partially immersed in solvent for a period of up to ten minutes and the degree of coating removal observed.

3. Experiments

3.1 Experiment 1

The original plan had been to leave the test specimens in the wet chamber (with the hydrogen sulfide and sulfur dioxide) for six days, then transfer them to the dry chamber (with ozone, formaldehyde, and ascetic acid) for one day, to dry out and stress the coatings. This alternating exposure schedule was intended to be repeated for several months. However, exposure to the sulfur pollutants was overwhelming, and caused noticeable to severe tarnishing of many test specimens by the end of the first six-day period. The level of H_2S in the test chamber fluctuated, up to 7 ppm; SO_2 was at a level of about 1 ppm. Experiment 1 was halted at this point, and all test specimens were evaluated for their ability to protect the silver from sulfur compound exposure.

The bent specimens and coins were cleaned and degreased, then recoated following our established protocols. New electrical resistance sensors and glass tubes were coated as before.

3.2 Experiment 2

3.2.1 Experiment 2A

The accelerated aging procedure was repeated with sulfur pollutants removed from the pollutant mix, to check for any affects the other pollutants might have, and to see how well the coatings performed under repeated wetting and drying. The alternating exposure schedule as described in Section 3.1 was conducted for three months. During this second experiment, pollutant levels were maintained at about 1 ppm for ozone, 10-25 ppm for acetic acid, and 5-10 ppm for formaldehyde. All visual and quantitative assessments were then performed.

3.2.2 Experiment 2B

The same test specimens from experiment 2A were then placed back into the wet chamber, and exposed to six days of high levels of hydrogen sulfide (3 ppm, without sulfur dioxide). The purpose of this exposure was to check whether or not aging of the coatings had an effect on their relative resistance to tarnishing by hydrogen sulfide.

4. Results

4.1 Experiment 1

The results of the two-way ANOVA test for visual differences between bent specimens is given in Table 1. In this case, 10 replicates for each of the three coatings (5 sprayed and 5 brushed) were ranked by three different individuals. Rankings were from best (least corroded, and thus with better protection offered by the coating) to worse (most corroded, worse protection offered by the coating). There were large differences visible between specimens (Figure 7).

Agateen was clearly the best coating for protection against sulfur exposure. The difference between it and the other two coatings is statistically significant ($p = 0.00$). The other two coatings are statistically similar to each other, although visually B-48N performed slightly better than did B-72. For all three coatings, spraying on the coating appears to be better for corrosion protection than brushing, and the difference is statistically significant ($p = 0.00$). There is a slight interaction effect, with the spraying versus brushing results a bit stronger for Agateen than for the two acrylics, but this difference is not statistically significant (which means that given the within-group variation, the between-group variation is not significant).

For the visual assessment of coins, the same ranking and statistical analysis procedures were performed. The results are given in Table 1. Again, Agateen was clearly the best-performing coating for protecting against sulfur exposure. The difference between it and the other coatings was statistically significant ($p = 0.00$). As before, the other two coatings were relatively similar in performance. Sprayed coatings and brushed ones showed no statistical difference, and no interaction effects were observed.

For the electrical resistance sensors, a baseline reading was taken prior to exposure to sulfur. At the end of the one week period, the sensors showed that Agateen provided better protection against tarnish from sulfur than did the other two coatings (Table 1). The difference in angstroms of metal lost was unexpected: for the four Agateen replicates, the average loss was 46 angstroms; versus an average of 190 for the B-72 replicates and 329 for the B-48N replicates. An analysis of variance shows this difference to be statistically significant ($p = 0.00$)

For the coatings applied to glass tubes, none of the three coatings showed a measurable reduction in light transmission prior to exposure to the "polluted" test atmosphere. This was true at all three wavelengths. From this it was concluded that all three candidate coatings are quite clear and transparent as applied.

After the first exposure period in high levels of hydrogen sulfide, all tubes showed some degree of white clouding to the naked eye. However, those coated with Agateen were relatively clear, while those coated with B-72 and B-48N were relatively opaque. Monochromatic transmission readings showed clear differences among the coatings, with the B-72 and B-48N coatings exhibiting a reduction in transmission of 16-26% versus the unexposed controls. The Agateen coating, on the other hand, showed only a 3-4% reduction as a result of the same exposure.

These results indicate that the high sulfur atmosphere is attacking the coatings themselves, as well as the underlying metal. All three coatings were easily reversible in acetone and/or xylene after the conclusion of the experiment.

4.2 Experiment 2A

The bent specimens and coins were assessed visually by the same protocols used in experiment 1. The results were similarly statistically analyzed by a two-way ANOVA as described above. Results are summarized in Table 1.

For the bent specimens, Agateen had a slightly lower overall score (indicating less tarnish) than did B-72, and B-48N; however, the differences were not statistically significant ($p = 0.70$). In contrast, application method was significant ($p = 0.03$), with brushing providing greater protection than spraying. There were no interaction effects between coating and application method.

For the coins, although not as dramatic in appearance as with the first experiment, Agateen again performed better ($p = 0.00$) than the other two coatings. There was no significant difference between B-72 and B-48N. Again, there was a significant difference overall between spraying or brushing ($p = 0.02$), with spraying providing better results. There were no interaction effects.

The electrical resistance data showed no serious corrosion development for any of the coatings upon exposure to this second environment (no serious loss of metal), and there is no difference in corrosion protection between coatings. The visual differences, then, may be due more to changes in the appearance of the coatings themselves.

New glass tubes had also been coated. Tubes that sat for the duration of exposure outside of the test chamber were used to separate the effects of time versus pollutants and cycling RH. These control tubes showed no measurable change in monochromatic transmission. For the tubes that underwent the three-month accelerated aging regime, all three coatings showed minor losses in light transmission, ranging from 12 to 15 % at 470 nm, 9 to 12 % at 580 nm, and 7 to 10 % at 650 nm. The changes observed for B-48N were somewhat higher than for the other two coatings; but all observed changes were small compared with those in Experiment 1. This result indicates that visual changes in the coatings themselves may be due more to incipient cracking and peeling.

Table 1 *Results*

		Applic.	Coating, Mean Values*			P-Values**		
Experiment	Substrate	Method	Agateen	B-72	B-48N	Coating	Method	Interaction
1	Bent	Brush	8	23	20			
		Spray	3	21	18	**0.00**	**0.00**	**0.08**
	Coin	Brush	4	9	6			
		Spray	3	8	9	**0.00**	**0.45**	**0.18**
	ER sensor	(Brush)	46	190	329	**0.00**	--	--
2A	Bent	Brush	10	14	12			
		Spray	18	16	23	**0.70**	**0.03**	**0.42**
	Coin	Brush	2	11	10			
		Spray	2	6	6	**0.00**	**0.02**	**0.17**
	ER sensor	(Brush)	94	119	99	**0.65**	--	--
2B	Bent	Brush	13	17	17			
		Spray	3	26	17	**0.00**	**0.75**	**0.01**
	Coin	Brush	4	7	5			
		Spray	2	11	8	**0.09**	**0.36**	**0.36**
	ER sensor	(Brush)	11	69	75	**0.00**	--	--

*Mean values are of ranks for bent specimens and coins, delta angstrom loss for ER sensors. Replicates are 10 for coating on bent, 4 on coins, 4 on ER sensors; and 5 for method on bent, 2 on coins.

**Statistically significant p-values are generally considered to be those at levels of .05 or below.

4.3 Experiment 2B

These results are also summarized in Table 1. For the bent specimens, Agateen performed significantly better (p = 0.00) than the other two coatings as a protective barrier against sulfur. For the coins, Agateen had a slightly lower score (less tarnish), although the difference is not statistically significant (p = 0.09). For B-48N and B-72 no differences were found between brushing and spraying for either test specimen type. For Agateen alone, spraying afforded better protection than brushing.

Sensors left from Experiment 1 were also re-exposed to this second sulfide atmosphere (except for one sensor that was destroyed in an attempt to see if it could be cleaned for re-coating). These results show a statistically significant difference between the coatings (p = 0.00), with Agateen causing less corrosion. The numerical values of additional metal loss were lower for all coatings than they were in the first exposure test, ranging from 8-104 angstroms (versus 11-388 angstroms). Again, all coatings were easily reversible after the conclusion of Experiment 2A/B.

5. Discussion

The primary objective of the experiments described above was to identify which of the three coatings performed the best. Indications of good long-term protective effects would include both serving as an effective barrier to harmful pollutants, and remaining intact through a variety of environmental stresses. Secondarily, we were interested in seeing if spraying or brushing made a difference and whether the coatings behaved differently on sterling silver bent coupons than with the engraved fine silver coins.

5.1 Experiment 2A

After experiment 2A, involving changes in RH and temperature and exposure to a variety of pollutants not including sulfur, most of the coatings were in good condition. However, a few were observed to be peeling along the edges of the bent specimens. Those that ranked worst showed slight yellowing of the coating. Those ranked highest were still a vibrant shiny strong silver color, with no yellowing or peeling. Visually ranking of the best and worst were easier than those in the middle, because there were few distinguishing differences between specimens.

For the bent specimens, all three coatings performed similarly in this second accelerated aging experiment with sulfur pollution removed. For the coins, however, Agateen showed less visual change. It is possible that this difference between performance with the bent specimens and coins may be due to differing effects of surface geometry, or to differences in composition of sterling silver versus fine silver.

Brushing was found to provide significantly better protection overall for the bent specimens, but not for the coins. It is possible that with the surface geometry of bending and extensive edges, spraying may sometimes lead to areas of incomplete or too thin coating coverage, which can be a significant problem after conditions of repeated long-term environmental stress. Electrical resistance data show that no serious corrosion development occurred, and there was no significant difference between coatings. The spectrophotometer readings of the coated glass tubes also showed that no major change occurred in light transmission through the coatings themselves. Thus any observed visual change may be mainly the effect of the slight cracking and peeling of the coatings from the substrates.

5.2 Experiments 1 and 2B

We can conclude that Agateen is distinctively the superior coating under exposure to high levels of sulfur. It shows the least deterioration, and provides a far better protective barrier against sulfur-induced corrosion. The performances of B-72 and B-48N are similar to each other, and it is not clear at this stage which would outperform the other. If protection against sulfur is a major concern, then Agateen is the recommended coating. Since Agateen also has handling and visual properties that many conservators prefer, this finding would appear to be a positive one.

After both experiments, the overall darkening of the silver on many test specimens (Figure 8) was considered to be failure. Electrical resistance sensors and coated glass tube analyses show that both tarnish development and increased coating opacity contribute to this visual change. In some cases where visible spots of tarnish developed, coatings were peeling. The peeling, however, was minor, and could perhaps be in part due to the tarnish disbonding the coating from below.

Although the electrical resistance sensors showed less metal loss for Agateen than for the two acrylics after both hydrogen sulfide exposures, that degree of loss was much less for Experiment 2B than it had been for Experiment 1. It is possible that this is due to somewhat lower concentrations of hydrogen sulfide, to the absence of sulfur dioxide, or perhaps the development of a very thin tarnish layer that may slow down subsequent rates of tarnishing. Still, the results of the first experiment with a high-sulfur atmosphere were replicated after the coatings had been subjected to three months of accelerated aging, and Agateen remains the better barrier against hydrogen sulfide relative to the other two coatings.

In these experiments, the only significant difference in application method for all coatings was seen on the bent specimens of Experiment 1, where spraying afforded better protection. Perhaps it produced a slightly thicker, more uniform coating, for better overall coverage, which helps protect the metal from hydrogen sulfide. For Experiment 2B, the improvement with spraying occurred only with Agateen.

Although spraying was found to be better for hydrogen sulfide protection, we found that brushing was better for the bent coupons of Experiment 2A. It may be that under longer-term conditions of environmental stress, sprayed surfaces will not hold up as well where there are many bends and edges. Since most artifacts have a complex geometry, brushing (with Agateen), while taking care to ensure there is complete coverage and a relatively thick coat, may be the best approach.

5.3 Comparison of Results to Real Case Studies

The results of this laboratory study were compared to observations of coatings after natural aging of historic silver objects. These observations included those of the objects conservator on our research team (D. Long) and those of other conservators as reported in the literature and on an online discussion forum.

Agateen has been used longer and more often in the conservation field as a silver coating than have the two acrylic coatings. No one has reported overall tarnishing of silver coated with Agateen, supporting our findings regarding impermeability. There have, however, been conflicting reports regarding its longevity. On objects coated with other cellulose nitrate lacquers, it has been observed that sometimes a deteriorated coating does not peel from the surface. Instead, as it shrinks, it leaves protection in small islands surrounded by uncoated surfaces that corrode rapidly.

However, the primary cause of coating failure observed with cellulose nitrate lacquers (as with any other coating used for a museum object) has been error in application; natural deterioration is also exacerbated by application errors. These errors include inadequate surface preparation; uneven application, with some coating areas being extremely thin; or areas being missed altogether, which is especially common in areas of complex geometry.

Heller (1983) was an early and strong advocate for Agateen, based on the ease with which it is possible to obtain a desirable quality of surface appearance. He reported observing Agateen-coated silver objects still in excellent condition after as long as 15 years, with no signs of deterioration. In trying to use B-72 as a silver coating, Heller found that solvents tended to evaporate more slowly, that spraying was especially difficult, and that the coating had a tendency to run and not level properly. The lengthy drying time made handling the object during application difficult, and the coating often remained soft and susceptible to fingerprints, lint from gloves, or to dust.

An interesting discussion among conservators regarding their experiences with Agateen, other cellulose nitrate coatings, and B-72 appears on the electronic discussion list of the American Institute for Conservation Objects Group (Objects Specialty Group Discussion List 1997). Many conservators reported using Agateen, because of its many positive qualities. One noted it is very easy to achieve a beautiful surface by brushing or spraying using Agateen. Another reported using it for protection of indoor metals because it is less vapor-permeable than the acrylics such as B-72, and because it dries in such close conformation with the surface it is applied to, unlike acrylics that tend to leave an "orange peel" surface.

Another conservator who reports having tried a wide variety of lacquers, spray applied, on indoor silver has found that Agateen is by far the most "forgiving" so that there is rarely any problem with either the "orange peel" look or with bubbles forming on the surface. This was found to be an especially useful property for the common situation in which coatings were applied by less experienced technicians, and saved retreatment of unsatisfactory work. Here the impermeable quality of Agateen was also crucial, because the collection it was being applied to was housed in an institution with a severe sulfur pollution problem. One conservator noted that Agateen remains soluble in acetone, and so can easily be removed if necessary. Several conservators had experienced easy removal of Agateen coatings that were 10-12 years old, finding it to be very soluble in acetone, even when degraded.

One conservator has retreated hundreds of pieces of silver that were lacquered with cellulose nitrate lacquers in the late 1950's through 1970's. He found that those aging lacquers exhibited brittle losses, underfilm tarnish, discoloration, and often had small patches of degraded lacquer which could not be removed without extremely aggressive localized mechanical abrasion which also removed some metal. However, it was unclear if any of those lacquers were Agateen, or one or more of the many other cellulose nitrate lacquers that have been on the market, such as Frigilene (Plenderleith and Werner 1971). His experience with acrylic coatings was that they worked well for copper alloys and ferrous metals, while silver was quite reactive, with the lacquer layers peppered with tiny spots of sulfide corrosion.

Some members of the discussion group felt that the positive qualities of Agateen outweigh any potential need to remove and reapply it at a later time. One felt that it would need to be replaced in about 20 years, as it might discolor before the film actually breaks down. However, another felt that it is difficult to justify a treatment that would require coating replacement every 20 years, as many institutions do not have adequate resources for retreatment.

Selwitz (1988) discussed the chemistry and properties of cellulose nitrate, and clarified why it is appropriate for use as an indoor coating. He noted that there is no reliable documentation regarding exactly how long such coatings should be expected to last; but that cellulose nitrate cast into films and kept out of bright light appears to have held up well for over 60 years. He noted that studies showing lack of stability of cellulose nitrate involved light exposures equivalent to 100-150 years in a typical museum situation; and used very high temperatures which cause decomposition of cellulose nitrate, especially in conjunction with surges in RH. The modes of decomposition observed in such experiments would not be observed in conditions of actual use of a cellulose nitrate coating on silver. These findings were supported by recent research on degradation of cellulose nitrate adhesives (Shashoua, Bradley, and Daniels 1992), where the degradation was found to be substantially retarded by the plasticizer, and a lifetime of 50-100 years was hypothesized as probable under normal museum conditions.

Sease et al (1997) have noted that application method can be very important, as even an impermeable lacquer can allow tarnish to penetrate if there are areas of incomplete coverage, pores in thin lacquer, or interruptions along edges. They observed black tarnish appearing on lacquered silver objects within six months of being placed in exhibit cases where sulfur had off-gassed from both case materials and from other artifacts housed with the silver ones. The black crystals appeared to be growing at breaks in the lacquer; crystals then pushed off sections of the coating, allowing a larger area of tarnish to form. They recommend applying multiple layers to ensure that the coatings are flawless. Other conservators also follow this procedure of applying two layers of a coating brushed or sprayed in opposite directions when possible, to better ensure complete coverage, no matter which coating is used or whether it is brushed or sprayed (Wharton 1997).

However, at one institution, the experience of conservators has been that B-72, whether brushed or sprayed on, in two or sometimes even three coats, cannot protect silver in the presence of sulfur pollutants. They have found that even with multiple coats B-72 is permeable to any hydrogen sulfide in the display (Podany 1998).

No matter how stable a coating, if it is permeable to hydrogen sulfide then a dangerous situation is set into place. Environmental conditions in exhibition and storage spaces must be constantly and carefully controlled to prevent accumulation of the pollutant at levels of 0.10 ppb or more. Higher levels, or combinations of hydrogen sulfide with other sulfur pollutants, must be completely avoided even for brief periods of time or tarnish is likely to develop. Then not only must the coating be removed and reapplied, the tarnish itself must be removed. This usually requires use of acidified thiourea (a known carcinogen) to chemically dissolve the silver sulfide, or abrasives (Wharton 1997). The latter create fewer health hazards, but can be extremely time consuming, and will remove some of the silver.

6. Conclusions

Our experiments clearly show that Agateen is much less permeable to hydrogen sulfide than are Paraloid B-72 and Paraloid B-48N. This fact holds true both for freshly coated silver and for those with deteriorating coatings. Where no deterioration has occurred, Agateen is remarkably impermeable to even extreme levels of hydrogen sulfide and sulfur dioxide; our findings coincide with field observations that have been made by conservators. Since levels as low as 0.10 ppb of hydrogen sulfide are known to tarnish silver, impermeability to this pollutant is an important consideration in coating selection. Removal of tarnish is a long and involved task, to be avoided if at all possible.

In an accelerated aging environment containing cycling RH and temperature, along with a pollutant mix, there was no significant difference in performance of the three coatings on the bent sterling silver specimens. All three began to peel and develop losses along edges and corners, and all three coatings developed noticeable discoloration. On fine silver coins Agateen continued to perform better. However, the overall black tarnish seen during exposure to sulfur pollutants did not appear under these experimental conditions. Electrical resistance measurements and spectrophotometer data indicate that the observed difference may be mainly due to differences in incipient cracking and peeling of the coatings.

Conservators frequently express concern over the stability of Agateen because of problems associated with other cellulose nitrate products, but primarily because of De Witte's 1973 studies which indicated cellulose nitrate coatings were much less stable than acrylics such as B-72. However, following the suggestion of Selwitz (1988) that the high temperatures used in those experiments would create problems not observed under normal use, less extreme aging conditions were used for our experiments. Our results indicating relative stability of Agateen when used in an indoor environment coincide with many observations reported by conservators who use this coating; however, based on such observations these results should not be extrapolated to other cellulose nitrate coatings. The mix of additives found in individual products may have important effects; and the known detrimental effects of ultraviolet radiation on cellulose nitrate should preclude its use in an outdoor environment.

Agateen has distinct advantages in ease of application and in surface appearance on silver. Given its performance in these tests, it clearly should have a place in the conservation of silver objects. B-72 and B-48N have more equivalent stability, reversibility, and protection from tarnish in the absence of sulfur pollutants. Their problematic working properties may be adjusted by changes in solvent, additives, or other aspects of formulation. However, they should only be used in an environment that can be guaranteed to be free of sulfur pollutants, or they will probably fail. It is possible that multiple layers of coating will ameliorate the problem with permeability, but it remains to be tested whether or not that will be effective and what the optimum thickness or number of layers would be. Reported experiences of conservators indicate that two to three layers as normally applied in conservation may not be sufficient for hydrogen sulfide-permeable coatings.

For any coating, inadequate surface preparation and applicator error is often the source for the initiation of tarnish. In our experiments we found that where there are many bends, narrow edges, and other geometric complexities, brushing rather than spraying provided better coverage for those difficult areas, and thus reduced peeling and cracking problems under environmental stress. But for hydrogen sulfide protection, spraying was sometimes more effective, perhaps resulting in an overall thicker and more uniform coating. To be safe, some conservators routinely apply two coatings to ensure better coverage; this is clearly a prudent step.

Many other coatings are available from manufacturers, and may produce superior results to those tested here. In addition to testing B-72 and B-48N applied in multiple layers, supplementary research could be done to evaluate other coatings for protection of silver housed indoors. Conservators having a wide repertoire of materials and techniques from which to choose for a specific situation, rather than a limited number of tested coatings, should be our ultimate goal.

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Suppliers

Electrical resistance sensors: Model 610 High Sensitivity Atmospheric Corrosion Sensor, Rohrback Cosasco Systems, Inc., 11841 East Smith Avenue, Santa Fe Springs, CA 90670.

Dräger tubes: Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA 15219-9919.

Agateen Lacquer #27 and #1 Lacquer Thinner: Agate Manufacturing Co., 11-13 Forty-third Road, Long Island City, New York, 11101.

Paraloid B-72 and B-48N: Röhm and Haas Company, Independence Mall West, Philadelphia, PA 19105.

Butyl Cellosolve: Aldrich, 1001 West Saint Paul Avenue, Milwaukee, WI 53233.

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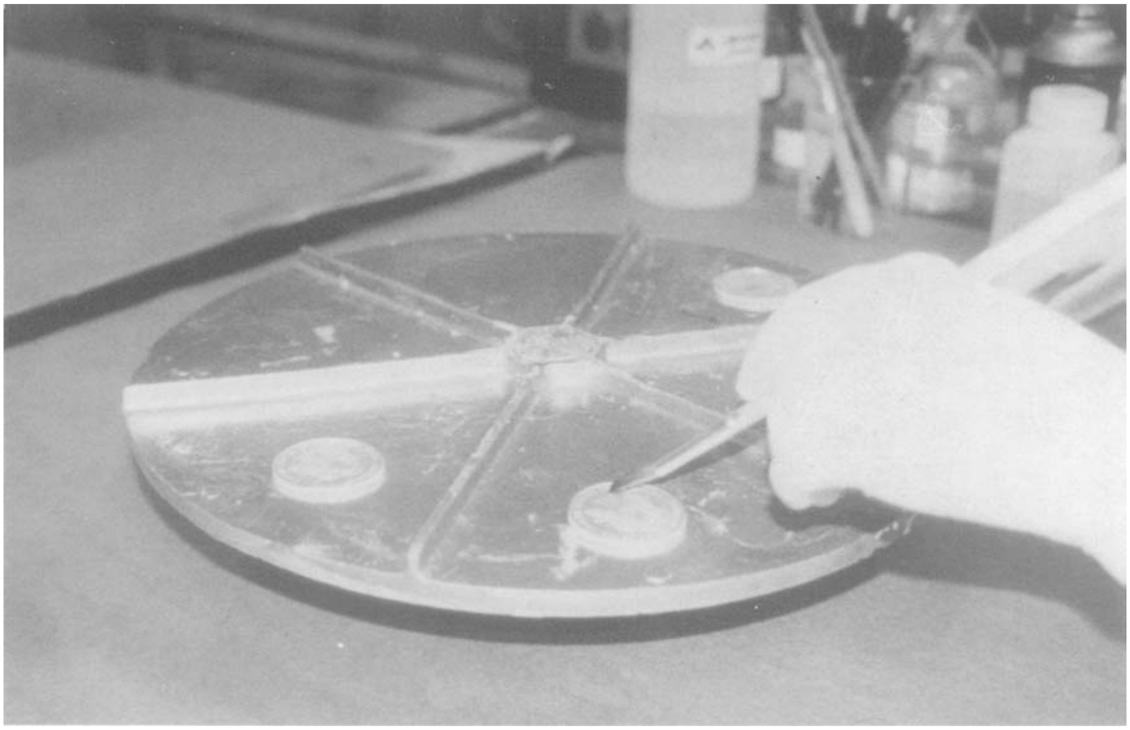

Figure 1. Brushing on coating with soft-bristled artist's brush.

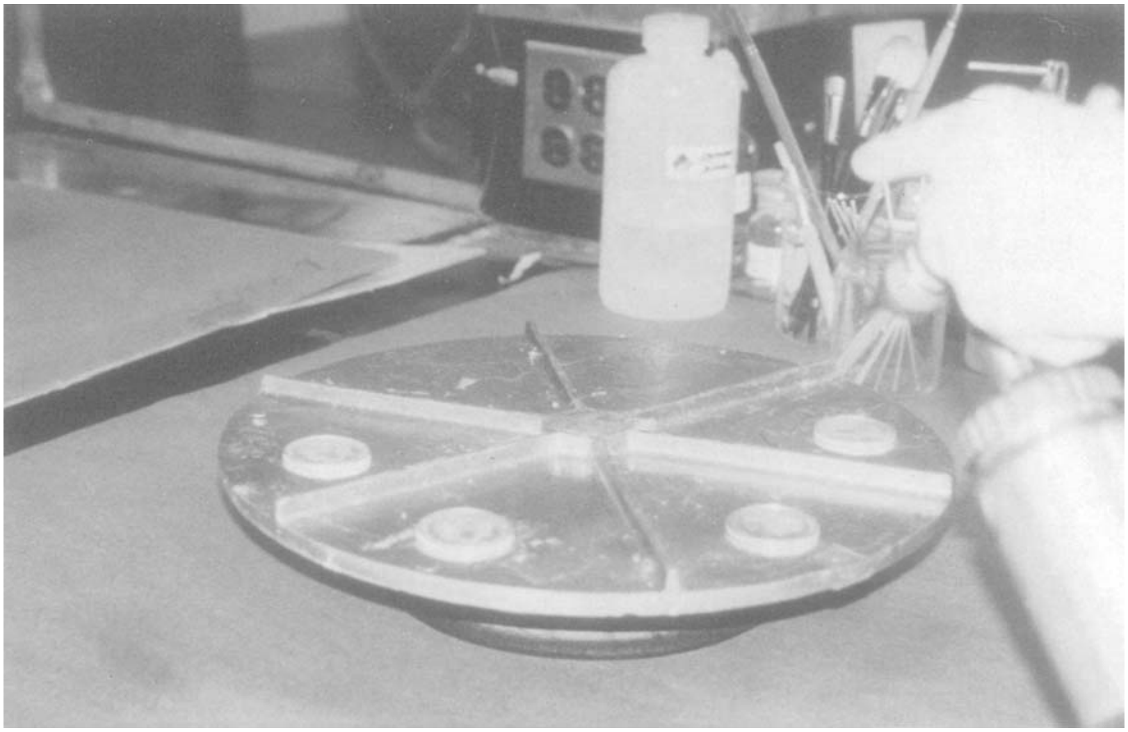

Figure 2. Spraying on coating with Devilbis spray gun at 20 psi.

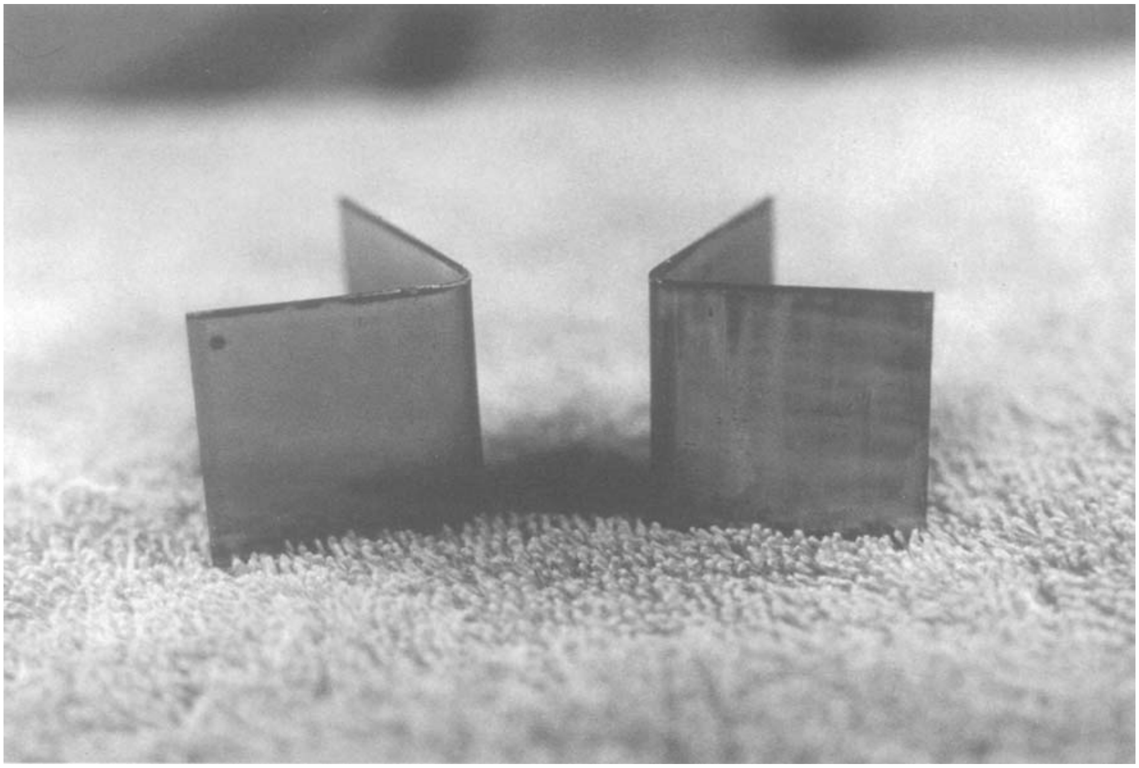

Figure 3. Bent sterling silver test specimens.

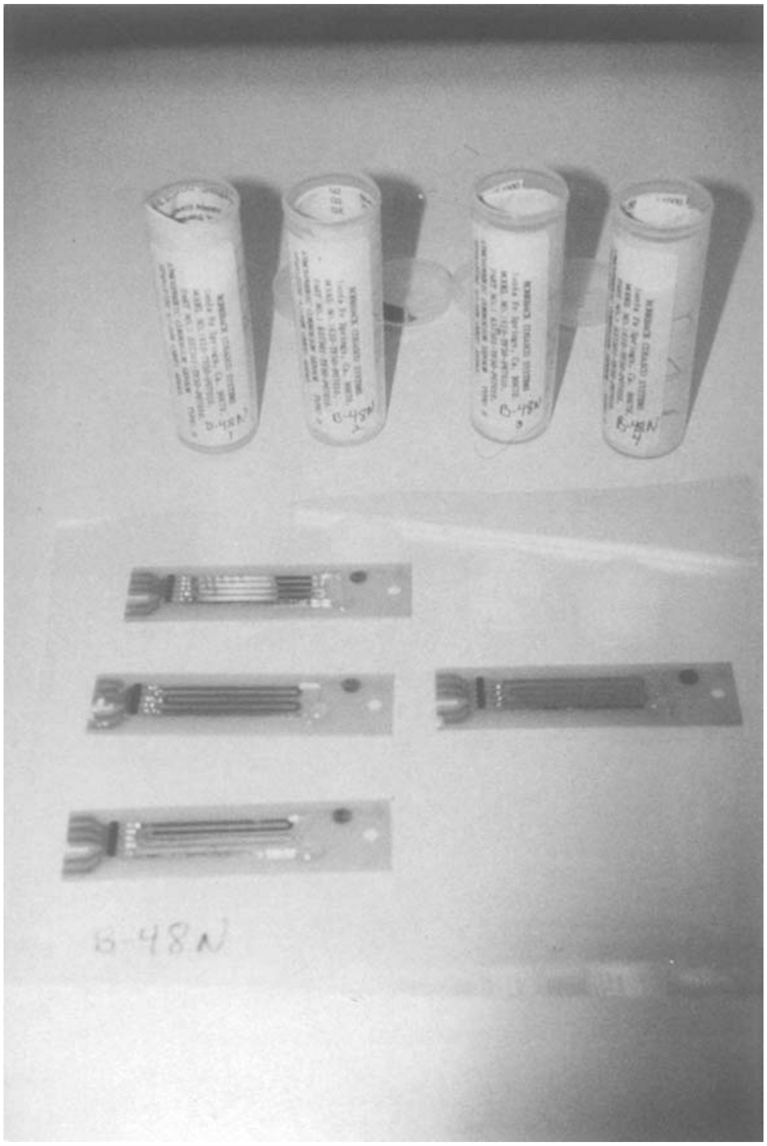

Figure 4. Electrical resistance atmospheric corrosion sensors.

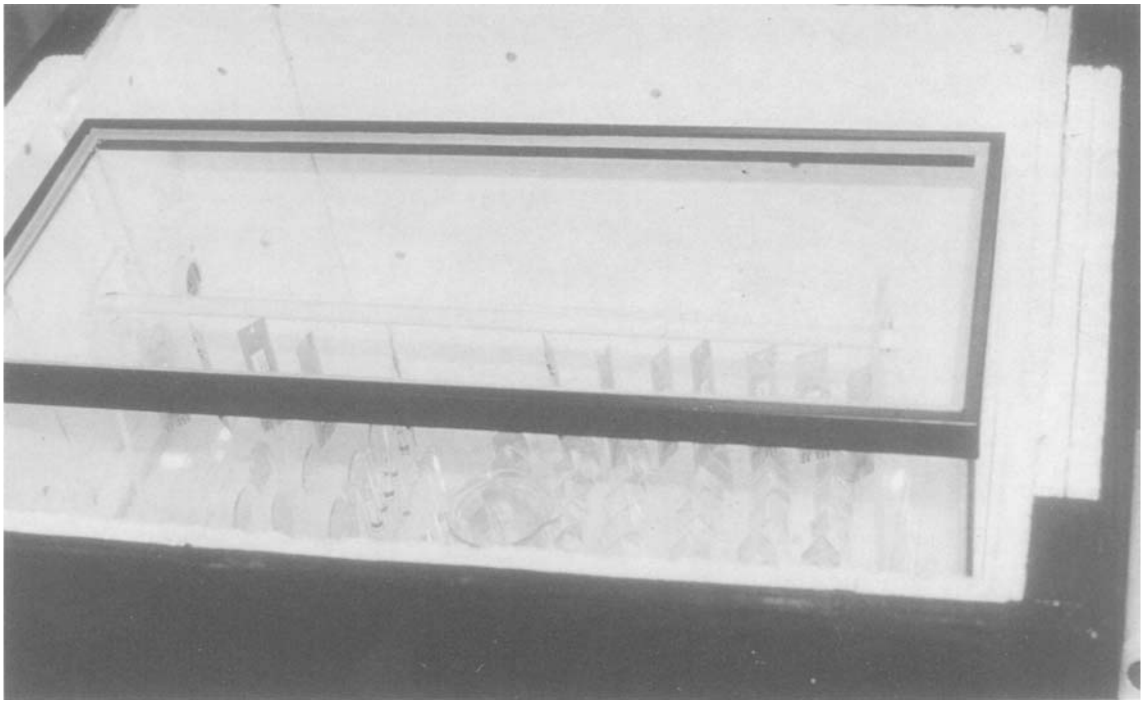

Figure 5. Accelerated aging chamber with removable sample holder in place.

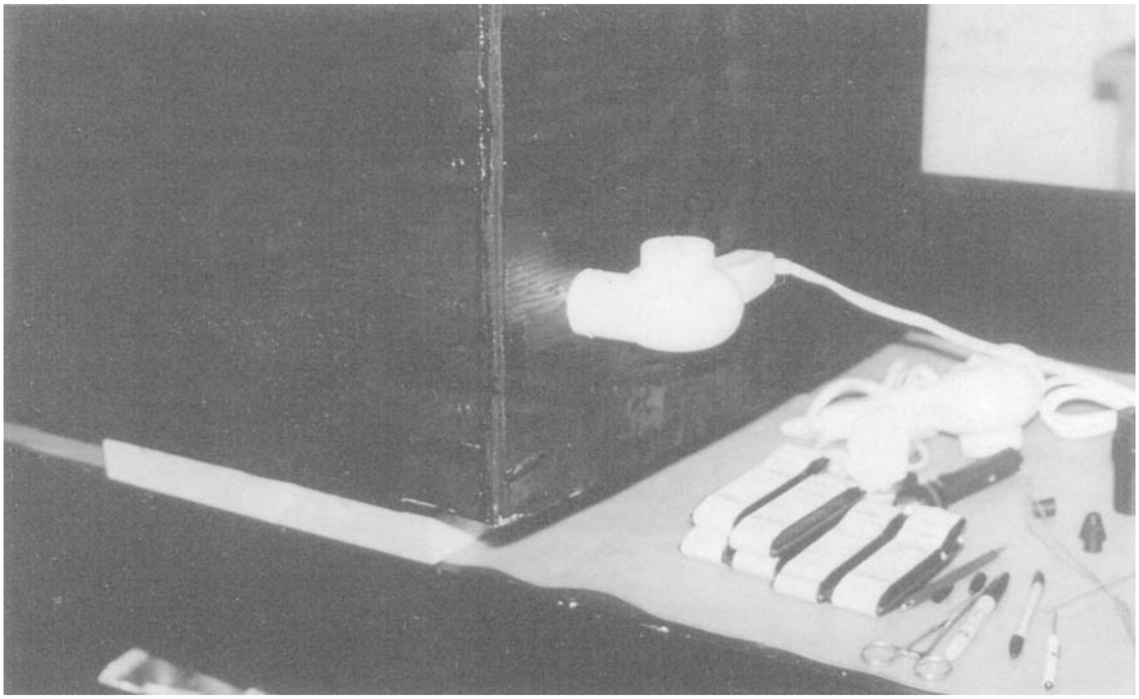

Figure 6. Hot air gun set into hole in plywood box surrounding the glass chamber.

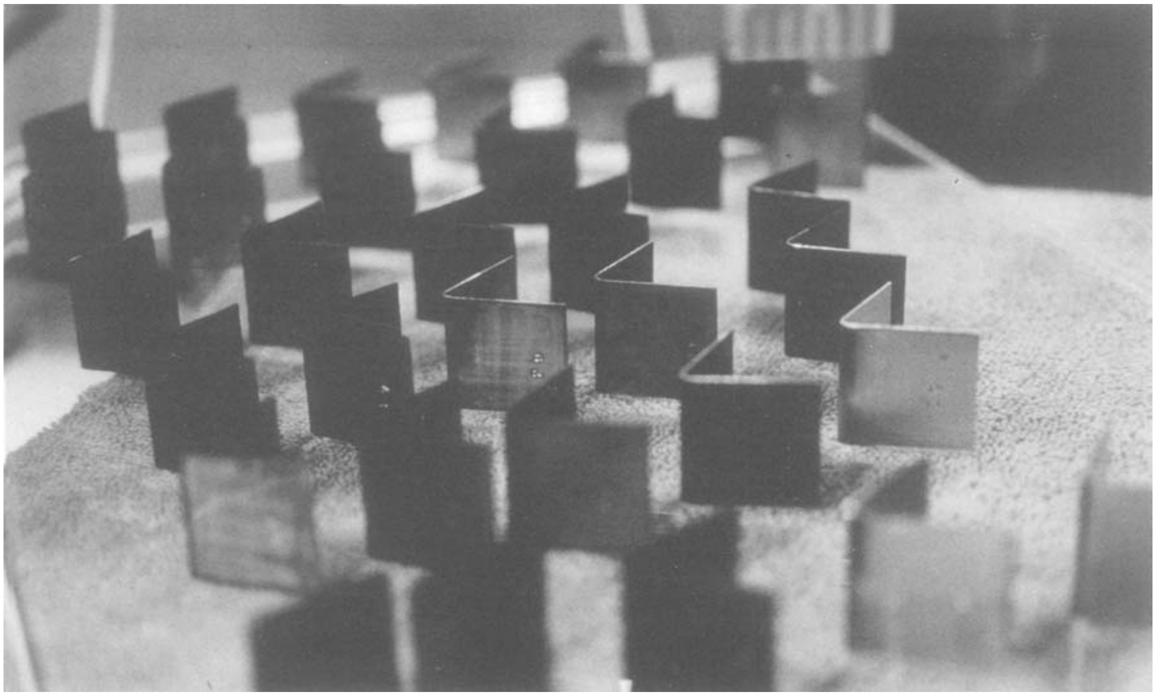

Figure 7. Bent coupons after Experiment 1, with large differences in tarnish levels.

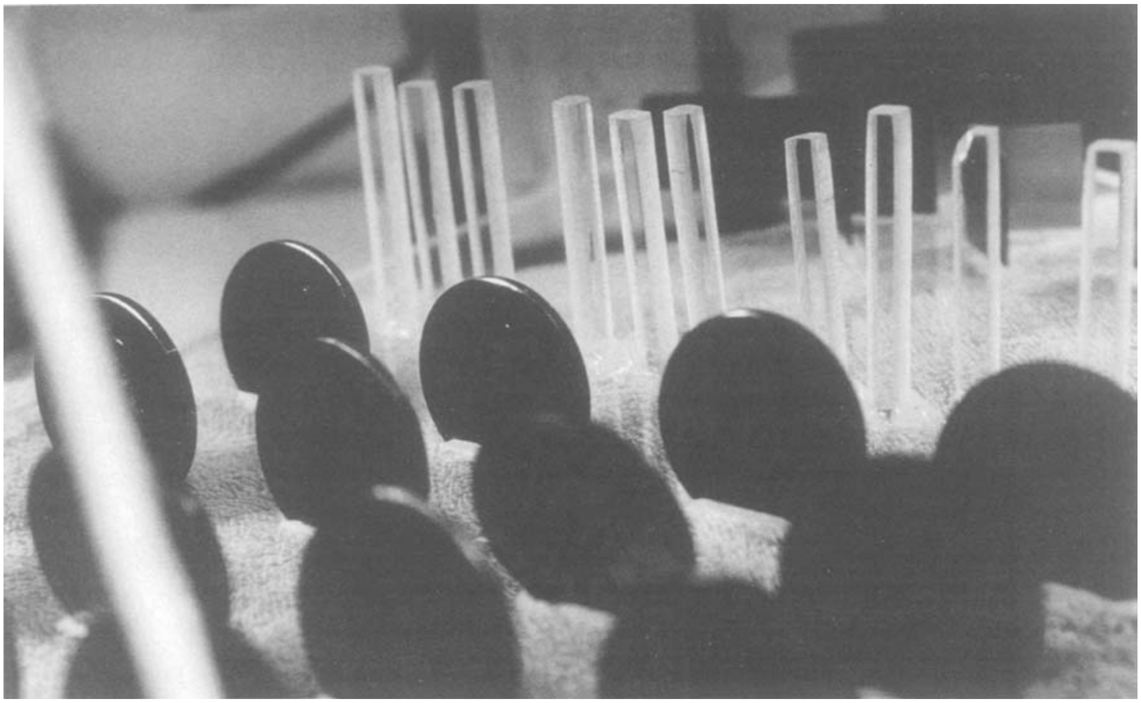

Figure 8. Overall darkening of silver coins after exposure to hydrogen sulfide. Coated glass tubes are also visible.

THE HIDDEN SECRETS OF COPPER ALLOY ARTIFACTS IN THE ATHENIAN AGORA

Alice Boccia Paterakis

Abstract

Four copper corrosion products on copper alloy objects in the Athenian Agora collection were analyzed by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy-Energy Dispersive Analysis Xray (SEM-EDAX), and Ion Chromatography (IC) at the British Museum. Blue/green corrosion was identified as sodium copper carbonate acetate, white crystals as sodium acetate trihydrate, a turquoise blue corrosion as copper (II) hydroxide spertinite, and a dark brown corrosion as cassiterite and cuprite. The factors which may have led to the development of these compounds are discussed which include cleaning and stabilization agents such as sodium hydroxide and sodium sesquicarbonate, and acetic acid from wooden storage materials. The influence the equilibrium Relative Humidity (egRH) of these compounds may have on continued deterioration leads to a consideration of methods for their removal.

1. Introduction

In 1998 blue/green corrosion on copper alloy objects was tentatively identified as a compound based on copper acetate by X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis (1). The XRD patterns of five samples were published for comparative purposes (1).

Further analysis of this blue/green corrosion and other corrosion products has been carried out by XRD, FTIR, Ion Chromatography (IC) and Scanning Electron Microscopy with Energy Dispersive Analysis X-ray (SEM-EDAX) at the British Museum. Thickett had identified a pale blue corrosion product on bronzes in the British Museum as sodium copper acetate carbonate (2,3,4). It has been determined that the build-up of acetic (ethanoic) acid emissions in wooden storage cupboards is a major contributor to the formation of this compound. The objects analyzed from the collections of the Agora and the British Museum had been stored in wooden cupboards since the 1930s. The acetic acid concentration in these wooden cupboards in the British Museum and Agora Excavations has been measured. A concentration of 1267 **µ**gm (500 ppb) acetic acid found in the Agora Excavations is comparable to the levels found at the British Museum: 1071 to 2880 **µ**gm^{-3} (1,2). Relative Humidity (RH) has been shown to play an important role in the corrosive activity of volatile acetic acid on metal (5). In the Agora Excavations the blue/green corrosion was found on a small percentage of the bronze collection and only on chemically stripped objects whereas in the British Museum it was found also on objects which retained their original corrosion products. In the Athenian Agora dark brown corrosion is often found on the surface of chemically stripped objects with the blue/green corrosion (1). It was hypothesized in 199$ that this dark brown corrosion might be copper (II) sulphide covelite or copper (I) sulphide chalcocite resulting from residual sulphuric acid from cleaning. Another explanation offered was the artificial patination of these chemically stripped objects with hydrogen sulphide followed by ammonia or acetic acid vapors (6). Other chemicals published for artificial patination consist of sodium sulphite or sodium thiosulphate solution (7) and sodium carbonate or bicarbonate (8).

White crystals are frequently found interspersed with the blue/green corrosion. It has been observed that these crystals develop after the formation of the blue or blue/green corrosion (8). Thickett and Tennent have identified these white crystals on objects in the British Museum and other collections as sodium acetate trihydrate (2,8). These crystals may take the form of needles or powder. Powder-like white crystals were present on those Agora objects sampled for blue/green corrosion.

2. Analysis

There was insufficient corrosion remaining from the objects analyzed in 1998 for further analysis so six other objects were selected from the Agora collection. Three objects were sampled for the blue/green corrosion, one for dark brown corrosion, and one for a turquoise blue corrosion. These were analyzed by XRD, FTIR, IC and SEM-EDAX at the British Museum.

2.1. Analytical Techniques

XRD samples the spacings between planes of atoms in a crystalline solid. The unique arrangement of atoms in a material generates a unique XRD pattern that can be used for identification. The use of a Debbye Schering camera allows analysis of samples as small as 1 microgram. Analysis was undertaken using Cu (alpha) radiation produced from an x-ray tube operating at 40KeV and 40mA.

FTIR samples the vibrational transitions of a material and can be used for amorphous as well as crystalline materials. Absorption patterns are unique and characteristic. The use of a beam condenser and diamond cell allows analysis of similar sample sizes to XRD. A Spectratech Sample plan diamond cell with a 4x beam condenser on a Nicolet Avatar 360 FAIR was used. The spectra were processed and searched using Nicolet Omnic ESP software and libraries developed by the British Museum and in collaboration with the Infra-Red Users' Group. A combination of both XRD and FAIR can be very powerful and allow a full identification to be made.

IC is a modification of liquid chromatography and can allow simultaneous determination of many anions and cations in solution including acetate. Analysis was undertaken with a Dionex DX300 system using an AS12A column with 2.7mM sodium carbonate and 0.3mM sodium hydrogen carbonate eluent for anions and a CS12 column with 20mM methane disulphonic acid eluent for cations.

SEM-EDAX can generate elemental analysis from extremely small samples (1 micron diameter). It can be sensitive and quantitative for all elements except boron and hydrogen. A Joel 840 SEM with Link analyzer system was used for this work.

2.1.2. Samples Analyzed from Copper Alloy Objects

#1 blue/green corrosion from unidentified object found in 1936 in a cistern
#2 blue/green corrosion from handle of a bucket found in 1937 in a well
#3 blue/green corrosion from unidentified object found in 1939 from mixed fill
#4 turquoise blue corrosion from bowl found in 1932, object completely mineralized
#5 dark brown corrosion from unidentified object found in 1939

Objects # 1, 2, 3 and #5 had been chemically stripped. It is not known what chemicals or methods were used to strip these objects although zinc and sodium hydroxide for electrochemical reduction are likely candidates. Object #4 was completely mineralized preserving the original corrosion products of cuprite and malachite. Although object #4 has not been chemically stripped it could have been treated with sodium sesquicarbonate. Dark brown corrosion and white crystals coexist with the blue/green corrosion on objects # 1, 2, and 3 in relatively small quantities. The blue/green corrosion and dark brown corrosion consist of a soft powder which was easily removed from the surface. The pale blue corrosion of object #4 is intimately bound to the surface of a layer of malachite, which rests on cuprite. It was removed with a scalpel attached to the malachite layer.

3. Results of Analysis

The blue/green corrosion (samples # 1, 2, and 3) has been identified as sodium copper acetate carbonate ($NaCu(CO_3)(CH_3COO)$, the same compound found on copper alloy objects in the British Museum (2,3,4). SEM-EDAX detected sodium copper carbon and oxygen as the major elements present. IC of a dilute sulphuric acid solution determined the presence of both acetate and sodium ions (copper and carbonate would not be detected with the instrument configuration used). The presence of carbonate was confirmed by effervescence with acid. The sodium copper acetate carbonate on Object #2 was found to be insoluble in water as was this compound in the British Museum (3). Sodium acetate trihydrate ($CH_3COONa.3H_2O$) was found on Object #2 which may reflect an abundance of white crystals in this sample (3,8). Both FTIR and XRD are insensitive to less than 5-10% of a material within a mixture. Sodium acetate trihydrate was confirmed with XRD and FTIR. Sodium acetate and sodium acetate trihydrate are water soluble (9). The turquoise blue corrosion (sample #4) has been identified as copper (II) hydroxide spertinite [$(Cu(OH)_2$]. This compound was indicated by SEM-EDAX and confirmed by XRD. The dark brown corrosion (sample #5) is mainly tin oxide, cassiterite (SnO_2), and copper oxide, cuprite (Cu_2O), with a trace of zinc. SEM-EDAX indicated mainly tin and copper with some oxygen and carbon and a trace of zinc. XRD confirmed cassiterite and cuprite.

4. Discussion

4.1. Blue/green Corrosion

The contribution of acetic acid emissions from wooden storage cupboards undoubtedly plays a major role in the formation of sodium copper acetate carbonate (samples 1,2,3). Acetic acid concentration, temperature and relative humidity are important factors in the formation of copper acetates on bronze objects and the higher these levels the greater the possibility. The concentration of acetic acid may have been much higher when the storage cases were new and it should be kept in mind that the objects have had up to 60 years in which to develop the acetate corrosion product. The RH in the Agora storeroom was monitored over a one year period and was found to reach a maximum RH of 82% in the winter months. Also, the buffering capacity of the wooden cupboards should not be discounted in the consideration of RH inside the cases. The sodium copper acetate carbonate found in the British Museum was observed to deliquesce at a RH of approximately 65% and the equilibrium Relative Humidity (eqRH) of sodium acetate trihydrate was found to be 75% (3).

Other sources of acetate could be vinyl acetate and polyvinyl acetate adhesives, lacquers and consolidants which were used in the 1940s, 1950s and 1960s (1). Perhaps the small percentage of objects which have developed the sodium copper acetate carbonate represent those treated with acetate-based polymers.

Sodium which contributed to the formation of sodium copper carbonate acetate in the Agora may derive from 1) the burial environment, 2) chemical cleaning agents such as Calgon (sodium hexametaphosphate), zinc and sodium hydroxide, alkaline Rochelle salt (5% sodium hydroxide and 15% sodium potassium tartrate), alkaline glycerol (15% sodium hydroxide and 40% glycerin), and 3) the stabilization compound sodium sesquicarbonate. Conservation treatment records of individual objects were not kept in the early years of the excavation.

One possible explanation for the formation of sodium copper acetate carbonate may be found in the use of sodium sesquicarbonate. The formation of cuprite, tenorite and sodium copper carbonate hydrate (chalconatronite) on copper alloys which have been treated with sodium carbonate or sodium sesquicarbonate is a well documented fact (10,11,12,13). The copper corrosion products are dissolved and the copper salts are redeposited as small crystals of sodium copper carbonate hydrate. Perhaps the sodium copper acetate carbonate found on some of the Agora and British Museum objects consisted initially of sodium copper carbonate hydrate which over the years in wooden cupboards took up acetic acid forming sodium copper acetate carbonate.

Another explanation for the formation of sodium copper acetate carbonate could be the incomplete reduction of the secondary copper corrosion products such as malachite during the electrochemical cleaning. Any remaining malachite would serve as a host for the formation of sodium copper acetate carbonate. Assuming that the majority of chemically stripped objects were completely reduced this would explain why only a small percentage of these artifacts in the Agora Excavation have developed the blue/green sodium copper acetate carbonate. Thickett has shown that the presence of sodium is necessary for the formation of sodium copper acetate carbonate (3). Most likely two factors are required: the incomplete reduction of copper carbonates and residual sodium from incomplete rinsing after cleaning. The formation of sodium copper acetate carbonate does not seem to be dependent on alloy type (3).

4.2. Turquoise Blue Corrosion

The turquoise blue corrosion (sample #4) was identified as copper (II) hydroxide spertinite, $Cu(OH)_2$. The spertinite was found to be insoluble in water as reported (9). This compound is duck-egg blue, unstable in the presence of carbon dioxide and water, and poorly crystalline (12). In the presence of carbon dioxide it has a tendency to change into copper hydroxy carbonates or, in the presence of chloride, into copper hydroxy chlorides (atacamite, paratacamite) (15). Under normal ambient conditions copper (I) hydroxide it will undergo dehydration forming cuprite (Cu_2O). If there is a significant amount of moisture present, i.e. in the pores of hygroscopic corrosion products on corroded bronze, the dehydration process will be minimized thereby stabilizing the copper hydroxide. A high ambient RH may contribute to the moisture present in the corrosion products. In addition to the significant presence of water two other factors may support its stability: 1) the localized pH and 2) the presence of a mixture of tin (II) and tin (IV) corrosion products on the surface and the presence of degraded metal underneath. MacLeod has found many hydroxy species associated with tin hydrolysis (15). An additional factor which may stabilize the copper hydroxide is the adsorption of SO_2. Only one other instance of copper hydroxide on a copper alloy object has been found in the literature and that was from a marine context (14).

The use of sodium sesquicarbonate on this object cannot be ruled out although sodium was not detected in the analysis. It is possible that copper (II) chlorides and copper hydroxy chlorides, formed from the oxidation of copper (I) chlorides in the corrosion matrix, could be hydrolized by sodium sesquicarbonate (depending on the hydroxide concentration in solution) forming copper (II) hydroxide (15). The fact that sodium and acetate were not detected on this object, which had been stored in the same conditions as the other objects, substantiates the theory that the presence of residual sodium may be necessary for the formation of compounds based on copper acetate in wooden cases (3).

4.3. Dark Brown Corrosion

Cassiterite (SnO_2) and cuprite (Cu_2O) were found to make up the dark brown corrosion (sample #5). The primary tin and copper corrosion products present in the original corrosion front would have been exposed by the removal of the secondary corrosion products on the surface during cleaning. The primary oxidation product of tin, Sn2+, is subjected to hydrolysis and can be precipitated or the tin (II) can be further oxidized to tin (IV) which can then undergo hydrolysis. Chemical cleaning of tin and copper corrosion products, and the removal of copper (I) chloride complexes (e.g. with sodium sesquicarbonate), results in the hydrolysis of soluble tin (IV) and copper (I) materials producing cassiterite and cuprite. In electrochemical reduction with zinc and sodium hydroxide any non-reduced secondary copper corrosion products, such as malachite, form cuprite (Cu_2O) and tenorite (CuO), which appear as a black, powdery corrosion (12). The tin corrosion products, which generally are not reduced to tin metal, would be hydrolized to produce cassiterite (15). The trace of zinc detected by SEM-EDAX may be a residue from the zinc and sodium hydroxide electrochemical reduction method.

While the dark brown corrosion and blue/green corrosion occur together they seem to form independently from one another. The only common factor in their formation appears to be sodium, for example from sodium sesquicarbonate, which could have contributed to the formation of cuprite from copper (I) chloride in the dark brown corrosion (12) and the sodium copper acetate carbonate (blue/green corrosion).

5. Conclusion

The possibility of ongoing corrosion caused by the deliquescence of the sodium copper acetate carbonate and the sodium acetate trihydrate should not be overlooked. If RH levels cannot be maintained below the eqRH of these salt compounds then the removal of these corrosion products should be considered. Their removal could be carried out in the dry, crystalline state by mechanical means or in the liquid, deliquescent state by rinsing with an appropriate solvent or by absorption into a poultice.

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DESALINATION PARAMETERS FOR HARAPPAN CERAMICS, PART 2

Harriet F. Beaubien

1. Introduction

Desalination has been a conservation focus at the site of Harappa, Pakistan, since the Harappa Archaeological Research Project began its excavations in 1986. Protocols were developed to track carefully the treatment of thousands of terracotta artifacts per year, modified over time based on observations about the process. Samples of efflorescent salts from a variety of objects were regularly brought to the Smithsonian Center for Materials Research and Education (SCMRE) for analysis by fellows and interns who staffed the on-site laboratory. But it wasn't until 1994 that a more systematic look at the desalination process was proposed. While at Harappa, Emily Kaplan and Katherine A. Holbrow designed an experiment to evaluate over a 10 year period terracotta samples that had been desalinated to various levels (Holbrow et al 1996). Using manifestation of damage, the experiment aimed to identify a level of residual salinity that was tolerable to the ceramics, i.e. a safe desalination endpoint. The motivation was a desire for efficiency, which at Harappa is shaped first by water usage. Because the local tap water is saline (measuring as high as 1500μSiemens/cm), water suitable for desalination is produced by electrical stills on site. Time efficiency was also a consideration given the constraints of a busy excavation season and the enormous volume of terracotta material to be desalinated.

This paper synthesizes the results to date of the long term study launched at Harappa in 1995 and of experiments that it inspired, carried out by the following SCMRE fellows and interns: Marie E. Svoboda and Tania E. Collas (1994-5), Catherine E. Magee and Ellen F. Rosenthal (1995-6), Susan B. Peschken and C. Mei-An Tsu (1996-7), Elizabeth C. Robertson (1997-8) and Joanne M. Boyer (1998-9). In the experiments, our on-site desalination protocol was followed, using static baths of distilled water, periodic water changes and conductivity meter readings to monitor progress.

2. Review of Experiments

2.A Conductivity Correlation Tests

Several tests were carried out to demonstrate some well-known aspects of conductivity (Beaubien and Robertson 1997). The readings in μS/cm are a measurement of current carried by salts in solution between the electrodes contained in the meter's probe. While the readings are clearly linked to the quantity of salts in solution, they are influenced by the water volume of the solution. Measurements produced by the same quantity of sodium chloride (NaCl) dissolved in different volumes of water, shown in **Table 1**, demonstrate the inversely proportional relationship of readings.

TABLE 1: **Conductivity in different water volumes**

	g	ml	μS/cm
NaCl	0.1	50	2600
	0.1	100	1200
	0.1	150	800
	0.1	200	600

Conductivity readings were not found to be comparable when the same gram weights of different kinds of salts were dissolved in the same volumes of water, as shown in **Table 2**.

TABLE 2: Conductivity of different salts

	g	ml	μS/cm
NaCl	0.1	100	1200
KCl	0.1	100	2200
$CaCl_2$	0.1	100	2000
$CaSO_4 \cdot 2H_2O$	0.1	100	1050
K_2SO_4	0.1	100	1700
Na_2SO_4	0.1	100	1600

It is tempting to extrapolate from a conductivity reading a more concrete expression of salinity, such as grams of salt in solution. The LaMotte conductivity meter operator's manual suggests we can convert the reading to total dissolved solids in parts per million, by multiplying by 0.7. Assuming water solution, ppm can then be translated into g/L by multiplying by 0.001. **Table 3** shows the amount of salt (in g/100ml) when calculated solely on the basis of conductivity (column 3).

TABLE 3: Salinity calculated from conductivity

	1 g in 100ml (meas)	2 μS/cm (meas)	3 g in 100ml calculated
$NaCl$	0.1	1200	0.084
KCl	0.1	2200	0.154
$CaCl_2$	0.1	2000	0.140
$CaSO_4 \cdot 2H_2O$	0.1	1050	0.0735
K_2SO_4	0.1	1700	0.119
Na_2SO_4	0.1	1600	0.112

The variations between calculated and measured amounts make it clear that conductivity cannot reliably be used to calculate grams of salt in solution. The exception would be if it were a single identified salt and its particular mathematical factor were known. However, this does not reflect the reality of the field, where salts will be unknown, mixed and vary by location.

Despite these peculiarities of conductivity measurements, we have nonetheless continued to use this method as a general measure of the progress of desalination and as a tool for comparison. From a practical standpoint, the ratios of ceramic weight to water volume (g:ml ratios) must be standardized in order for the conductivity readings to be meaningfully compared. Where different ratios have been used in the same experiment, we have mathematically adjusted one set of measurements (using the inversely proportional relationship) for the sake of comparison.

2.B Desalination Efficiency Experiment

Different ratios of ceramic weight to water volume was one of the variables in an experiment examining efficiency aspects of the desalination process (Peschken 1997); two were selected to approximate the most parsimonious usage at Harappa, at 1g:1.5ml and at 1g:2.5ml. A second variable was the frequency of bath changes, comparing the progress of desalination if baths were changed daily with those changed only when the conductivity had leveled off (equilibrium). In this experiment, twenty sherds were each subdivided into four relatively equal parts and the parts from each were sorted into groups (A-D) for desalination. The results for each group are presented in **Table 4**, showing the number of baths and time required to reach conductivity levels of approximately 150μS/cm. Water efficiency is expressed as a product of the number of baths and the water volume unit per gram.

TABLE 4: Desalination efficiency to reach target conductivity of ~150μS/cm

Group, with desalination variables:	# baths	total water units/g (# baths × ml)	total time
A: daily @ 1g : 1.5ml	5	7.5	~ 5 days
B: equilibrium @ 1g : 1.5ml	6	9	> 2 weeks
C: daily @ 1g : 2.5ml	4	10	~ 4 days
D: equilibrium @ 1g : 2.5ml	5	12.5	~ 2 weeks

In this experiment, the equilibrium method offered no strong advantage in water efficiency, and the extended time needed to reach low conductivities would be impractical in a field situation, effectively eliminating it from consideration. Of the two groups changed daily, the one at 1g:1.5ml might be favored over the 1g:2.5ml group for its greater water efficiency in reaching a target conductivity. However, several factors argued for the latter. The fewer bath changes would offer a time savings from a procedural standpoint, and less risk to the objects from the standpoint of amount of handling. Additional information from several salt trend experiments also argued for fewer baths and shorter time.

2.C Salt Trends Experiments

A preliminary study which examined the trends of salts going into solution over the course of desalination was carried out using a sherd and a bangle fragment in several pieces [Collas 1995]. These were desalinated individually at a 1g:2ml ratio and the wash water was saved from each bath; these were then evaporated and the residues analyzed.

Because of its larger size, Sherd M1 produced residues in sufficient quantity to allow five baths to be analyzed; weight loss after desalination measured 2.65%. **Figure 1** shows the conductivity readings at each of the bath-change points, along with results of analysis by energy-dispersive X-ray spectroscopy (EDS) for semi-quantitative identification of elements, and X-ray diffraction (XRD) for identification of minerals. The chlorides of sodium (Na) and potassium (K) are prominent in bath 1 and 2, diminishing to minor status in the subsequent baths. The calcium salts, primarily calcium sulfate dihydrate (or gypsum), emerge and then dominate the later baths.

An expanded version of this experiment utilized material collected in 1995 during the processing of Group F in the desalination parameters experiment at Harappa (Tsu 1997). This group, composed of 1cm-long segments from 60 different bangle fragments, required ten baths at a 1g:2ml ratio to reach "0" conductivity (measured as <20μS/cm). From each bath container, the

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These data show that the highly soluble salts formed from sodium and potassium, chloride and sulfate ions dominate the first three baths. They continue to be detectable in subsequent baths, supporting earlier observations using the scanning electron microscope (SEM) of NaCl remaining in pores of completely desalinated bangles (Holbrow et al.1996, p. 73; also Willey 1995). The XRD and EDS data show that from bath 4 onward silicon-based compounds (notably quartz) emerge and remain prominent. These insoluble siliceous compounds in the bath residues give some indication that the ceramic paste itself is disaggregating, damage that can be ascribed to prolonged soaking.

2.D Real-time Aging Experiment

Damage caused by residual salts is being evaluated in an ongoing experiment intended to help identify a safe desalination endpoint. During the 1995 field season, 60 bangle fragments were collected, each of which was sawn into six 1cm segments, labeled and distributed into groups. These groups were desalinated at a 1g:2ml ratio with daily changes of water to the following conductivity levels (in μS/cm): 400, 300, 200, 100 and 0 (Group F), with an undesalinated control. That same year, an accelerated aging test carried out at SCMRE on some test bangle samples produced obvious damage only on the undesalinated controls (Svoboda 1995). This suggested that it might be prudent to include in the long term experiment samples whose desalination was terminated at levels higher than 400. During the 1996 field season, the study was expanded to include similarly processed groups of bangle segments desalinated to 500, 1000, 1500 and 2000, plus another set of undesalinated controls. Most of the samples are stored in open cups except for five from each group, which are stored in closed polyethylene bags, to simulate the typical storage conditions of terracotta material on site, as seen in **Figure 4**. The original set has now been aging for more than 4 years, the expanded set for more than 3.

The samples are examined and evaluated annually by SCMRE laboratory personnel using two principal methods, as originally proposed: weight changes and visual changes.

Weight changes

Table 5 shows selected weight data for samples in groups A through F, with weights (in grams) before and after processing in 1995 in column 1 and most recent weights in column 3. The loss initially experienced by Groups B through F (column 2) is primarily attributable to the removal of salts, with only minor fluctuations recorded since then; weights in 1999 were the same as those in 1998. The only group to show progressive weight loss since its original processing is Group A, the undesalinated control, as seen in column 4.

TABLE 5: Weight data in grams

Group, with μS/cm level	1 Wt. 1995		2 Δ_w BT-AT	3 Wt. 1999	4 Δ_w AT-1999	5 Total Δ_w BT-1999	6 Δ_w in % BT-1999
	BT	AT					
A: control	17.4	17.3	-0.1	16.9	-0.4	-0.5	-2.87 changing
B: 400	15.6	14.9	-0.7	15.1	+0.2	-0.5	-3.21 stable
C: 300	15.5	14.9	-0.6	14.9	--	-0.6	-3.87 stable
D: 200	15.7	14.8	-0.9	15.0	+0.2	-0.7	-4.46 stable
E: 100	14.5	13.8	-0.7	13.9	+0.1	-0.6	-4.14 stable
F: 0	15.6	14.9	-0.7	15.1	+0.2	-0.5	-3.21 stable

In an unfortunate oversight, the weights before and immediately after desalination for Groups H-M (those terminated at the higher conductivity levels) were not recorded. However, they have remained unchanged in the last two years except for continuing loss recorded for the control Group M.

Given that some of the weight variation may be due to moisture content differences (depending on residual salts and ambient humidity at the time), weight change has not been a sensitive enough indicator of damage except for the undesalinated controls, notably Group A. For these samples, weight loss may be easily explained by surface material that has flaked off in the bottom of the cups (noted also in the accelerated aging study [Svoboda 1995]), apparent as early as the 2-year point.

Photomicrographs taken of bangle sample surfaces with various types of salts serve as standard references. Three types are identified: fine white salts efflorescing in small clumps, often associated with reddish discoloration in the ceramic fabric (possibly an optical effect from localized salt concentration and deliquescence); compact crusts ranging from clear and shiny to whitish and opaque; and small reddish-brown spots discoloring the surface, often in dense concentrations.

The undesalinated controls provide ample evidence of the first two varieties, manifesting mostly on exterior (rather than cut) surfaces. The fluffy salts **(Figure 5)** have developed predominantly on the samples stored in cups, correlating with the occurrence of powdered ceramic material in the bottom of the cups. Crusts have developed on samples stored in both cups and bags, with crusts from the latter tending to be clear and shiny in appearance; a whitish example **(Figure 6)** was analyzed as calcium sulfate dihydrate (gypsum) by XRD. Some buildup of crust is evident on samples terminated at higher conductivity levels (e.g. 2000), but becomes harder to detect at lower levels (e.g. 400), particularly if relying on the naked eye alone.

The third variety of salts appears as brownish spots which when concentrated can generally be seen without magnification (**Figure** 7). These are similar to a phenomenon long noted at Harappa: undesalinated terracottas that had dried, but were bagged while still damp or stored in places with limited air circulation, often were covered with a sprinkling of fine brownish spots that disappeared with desalination (**Figure 8**). Several samples of the spots were identified by XRD as sodium chloride and a potassium-sodium chloride. In the case of a group of figurine fragments left out in the sun just prior to being immersed in water, it was noted that the spots began transforming into more typical whitish efflorescence. In the experiment, concentrations of the reddish-brown spots are recorded on several samples desalinated to intermediate levels, including one at 400 stored in a bag whose counterpart stored in a cup (from the same initial bangle fragment) shows isolated crystal clumps.

In an experiment which has attempted to limit variables by selecting a large number of samples of a single type and firing range, considerable variation and ambiguity exist within the groups at every level of desalination, even with magnification. These inconsistencies can be seen in the assessments of a standard set of 10 samples from each group (**Figure 9**). Thus far, only the undesalinated controls show damage which is easily visible with the naked eye. Using magnification, most of the samples desalinated to 200 and below appear to have surfaces as "good" as the fully desalinated samples. At conductivity levels higher than 300, nearly a third of the samples are "poor," with increasing numbers rated as "ambiguous." At the same time, a number of samples at the higher levels still appear good. The remaining years in this ten-year study may be necessary to produce a clearer indication of a safe level at which to terminate desalination.

3. Implications for Desalination Protocols at Harappa

While there remains the larger question of whether these samples with their small size and mass:surface ratio are representative of the desalination experience of pot sherds, a vessel or dense terracottas, the results of these experiments suggest the following refinements to our desalination protocols at Harappa. A daily change schedule of static baths continues to be a practical framework. Bath water volumes should be as generous as possible, within the severe constraints of availability, in order to favor a shorter period of desalination. Most importantly, desalination should be terminated after 4 or 5 days, as suggested by the expanded salt trends experiment. At this point damage to the ceramic itself may be occurring based on the emergence of silicon-bearing compounds, in contrast to previous baths in which soluble salts prevail. Even at bath 4, approximately 97% by weight of the total material released during desalination would have been collected. In nearly all of the experiments, conductivity at bath 5 was below 200μS/cm (as measured in baths at 1g:2ml ratios), a level that our real-time aging experiment after 4 years still suggests is "good."

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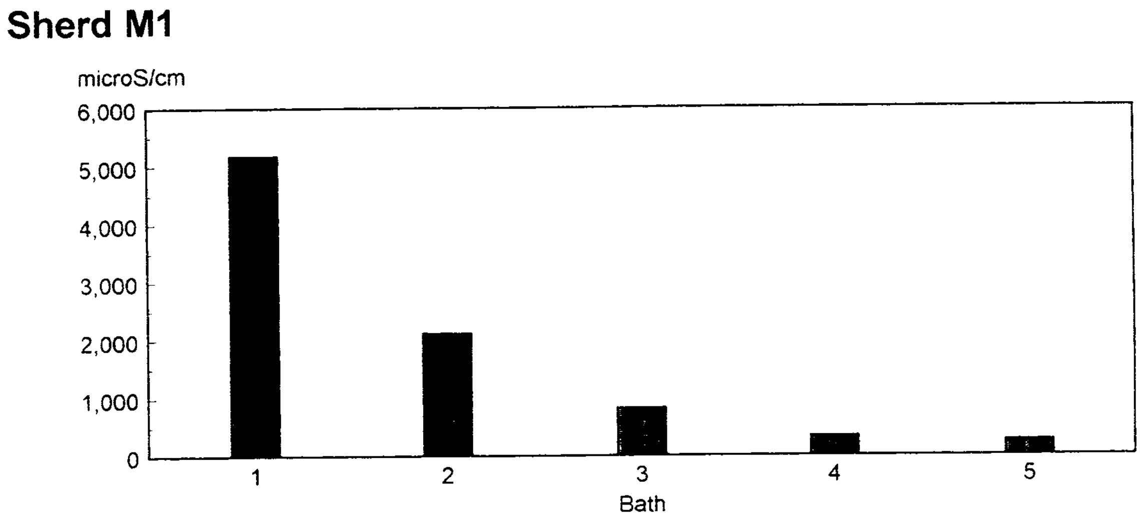
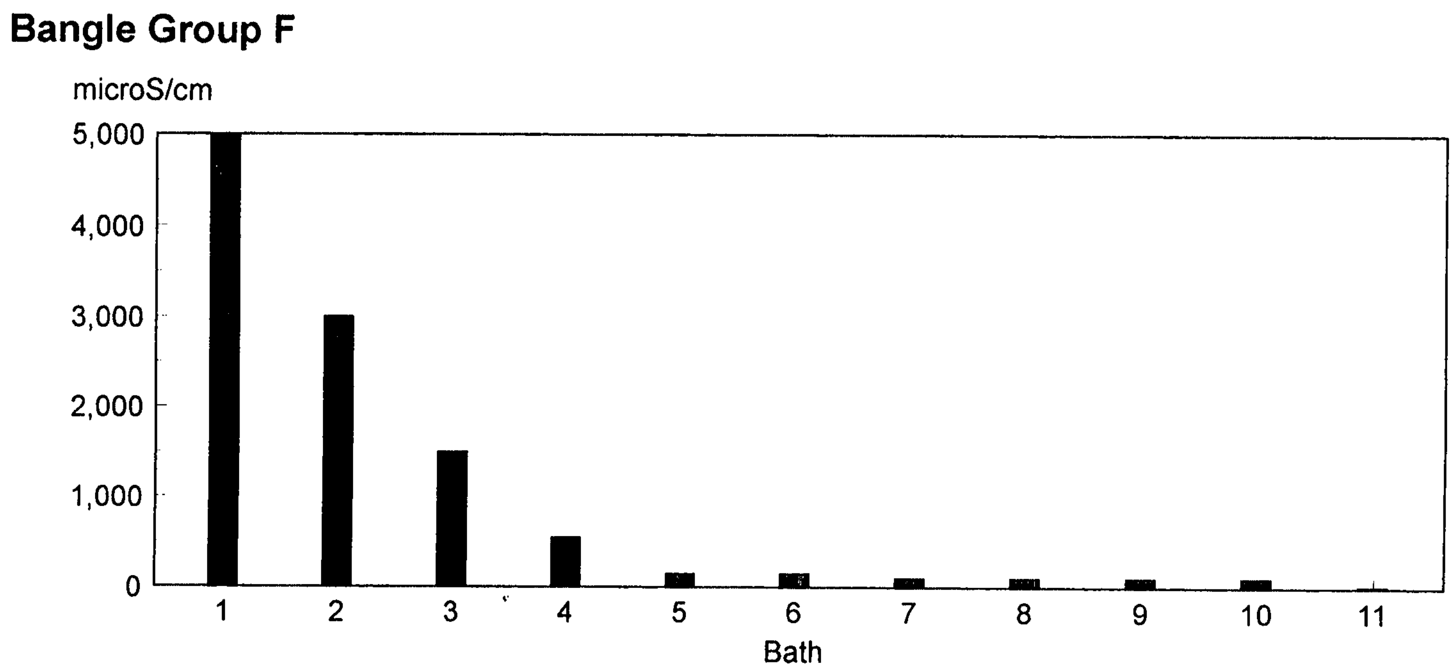


Conductivity	5180	2130	830	335	260
EDS major	**Na K Cl**	**Na K Cl**	**Ca S**	**Ca S**	**Ca S**
mid	C	S O C	Na K O	K	
minor	Si Mg S O	Ca Si Mg	Si Mg Cl C	Na Si Mg Al C O	Na K Si Mg Al C O
XRD	**NaCl KCl**	**NaCl** $CaSO_4$• $CaCO_3$	**$CaSO_4$•** $CaCO_3$ NaCl KCl	**$CaSO_4$•**	**$CaSO_4$•**

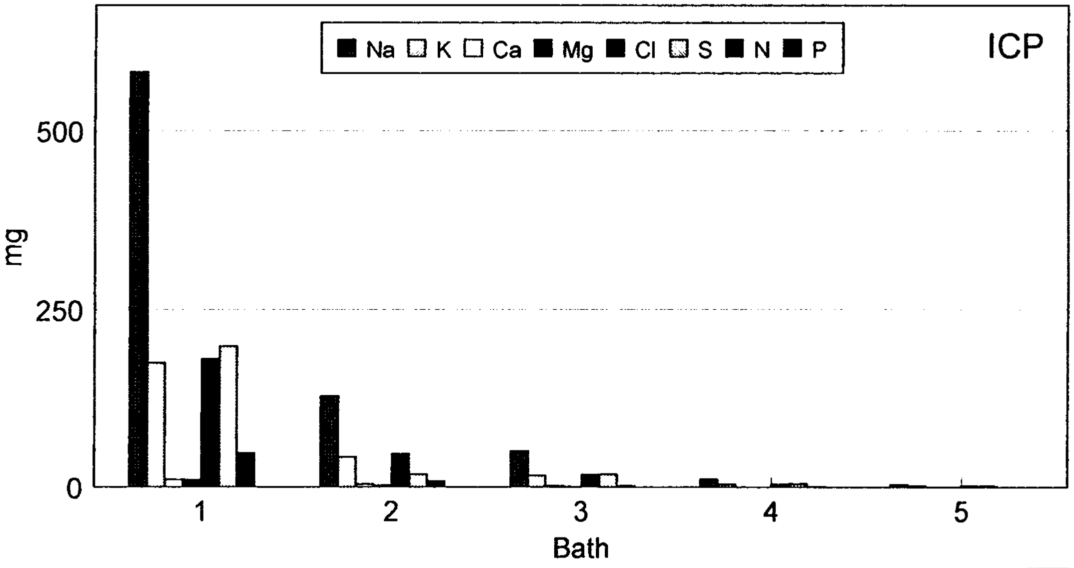
Figure 1. Sherd M1. Conductivity readings at bath changes (desalination ratio of 1g:2ml) and analysis of residues from each bath using EDS and XRD.



Conductivity	>5000	3000	1500	550	150	150	>100	<100	<100	100	20
Residues T=2.93g	**2.06**	**0.49**	**0.17**	**0.11**	**0.02**	**0.015**	**(<.01)**	**0.01**	**0.02**	**0.03**	**--**
% by wt. of total	70.3	16.7	5.8	3.8	0.7	0.5	(<.01)	0.3	0.7	1.0	--
% by wt. collected after 2, 3, 4 and 5 baths	87.0%		▨	▨	▨	▨	▨	▨	▨	▨	▨
	92.8%			▨	▨	▨	▨	▨	▨	▨	▨
	96.6%				▨	▨	▨	▨	▨	▨	▨
	97.3%					▨	▨	▨	▨	▨	▨

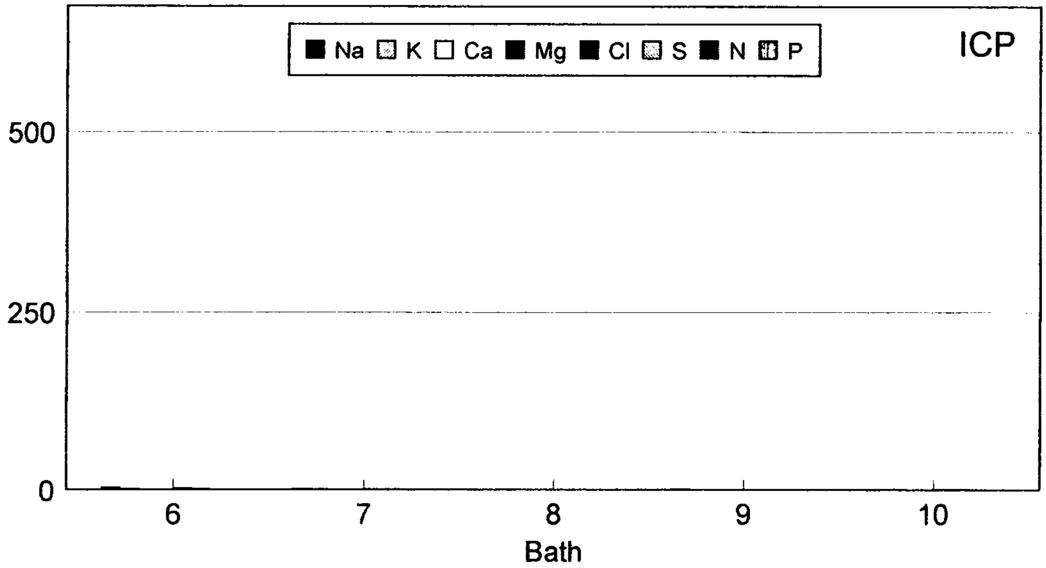
Figure 2. Bangle Group F. Conductivity readings at bath changes (desalination ratio of 1g:2ml) and weights of residues from each bath.

Bangle Group F



Residues (mg) (T=2925.52mg)		2060.4		494.4		170.6		108.1		28.4
ICP	wt%	mg	wt%	mg	wt%	mg	wt%	mg	wt%	mg
Na	28.25	582.07	25.90	128.07	29.59	50.48	10.30	11.14	13.81	3.92
K	8.48	174.80	8.56	42.33	9.67	16.50	3.96	4.28	6.19	1.76
Ca	0.52	10.62	0.85	4.19	0.97	1.66	0.23	0.25	0.05	0.02
Mg	0.48	9.93	0.53	2.62	0.38	0.66	0.06	0.06	0.03	0.01
Cl	8.76	180.42	9.40	46.43	10.27	17.53	3.95	4.27	7.12	2.02
S	9.62	198.20	3.70	18.29	10.73	18.31	4.21	4.55	7.28	2.07
N	2.32	47.90	1.68	8.31	1.12	1.91	0.46	0.50	0.17	0.04
P	0.01	0.07	0.01	0.04	0.01	0.02	0.04	0.04	0.03	0.01
EDS **major**	**Na K** **Cl S**		**Na K** **Cl S**		**Na K** **Cl S**		**Si Al**		**Si Al**	
intermediate					Si		Na K Cl S		Na K Cl S	
minor	Si Al Ca Mg O C		Si Al Ca Mg O C		Al Ca Mg S O C		Ca Mg Fe O C		Ca Mg Fe O C	
XRD	**NaCl** **$K_3Na(SO_4)_2$**		**NaCl** **$K_3Na(SO_4)_2$**		**NaCl** **$K_3Na(SO_4)_2$**		**SiO_2** NaCl $K_3Na(SO_4)_2$		**SiO_2** NaCl $K_3Na(SO_4)_2$	

Figure 3a. Bangle Group F. Analysis of residues from baths 1-5 using ICP, EDS and XRD. Approximately half of each residue was used for ICP; elemental concentrations for the total (in mg) were extrapolated based on measured weight %s.



Residues (mg) (T=2925.52mg)	**19.1**		**15.0**		**(2.3)**		**7.2**		**19.7**	
ICP	wt%	mg	wt%	mg	wt%	mg	wt%	mg	wt%	mg
Na	14.93	2.85	9.72	1.46	0.44	0.01	9.24	0.67	5.71	1.1
K	7.64	1.50	5.75	0.86	0.39	0.01	6.50	0.47	3.80	0.75
Ca	0.13	0.03	0.13	0.02	0.13	<0.01	--	**	0.24	0.05
Mg	0.06	0.01	0.03	<0.01	0.01	<0.01	--	**	0.07	0.01
Cl	9.13	1.74	5.36	0.80	0.45	0.01	4.10	0.30	3.61	0.71
S	8.62	1.65	4.90	0.74	0.41	0.01	4.02	0.29	3.58	0.71
N	0.03	<0.01	--	-0-	--	-0-	--	-0-	--	-0-
P	0.03	0.01	0.03	<0.01	--	**	0.05	<0.01	0.04	<0.01
EDS **major**										
intermediate	Si Na K S		Si Na K S		Si		Si Na K S		Si Na K S	
minor	Al Ca Mg Fe Cl O C		Al Ca Mg Fe Cl O C		Na K Al Ca Mg Fe Cl S O C		Al Ca Mg Fe Cl O C		Al Ca Mg Fe Cl O C	
XRD	SiO_2 muscovite* - NaCl - $K_3Na(SO_4)_2$		SiO_2 muscovite* - NaCl - $K_3Na(SO_4)_2$		SiO_2 muscovite* $K_3Na(SO_4)_2$ - NaCl		$K_3Na(SO_4)_2$ - SiO_2		SiO_2 - NaCl - $K_3Na(SO_4)_2$	

*$(K,Na)(Al,Mg,Fe)_2(Si_{3.1},Al_{0.9})O_{10}(OH)_2$

Figure 3b. Bangle Group F. Analysis of residues from baths 6-10 using ICP, EDS and XRD. Approximately half of each residue was used for ICP; elemental concentrations for the total (in mg) were extrapolated based on measured weight %s. Bath 8 was partially lost during initial processing.

Figure 4. Real-time aging experiment (February 1999). Samples are stored in large cups by desalination group (small cups are subsets of these), with some in closed polyethylene bags (upper right corner). Group A samples (undesalinated control) show white fluffy salt efflorescence (large cup near the lower left corner) and delaminated ceramic surface (small cup in the lower right corner).

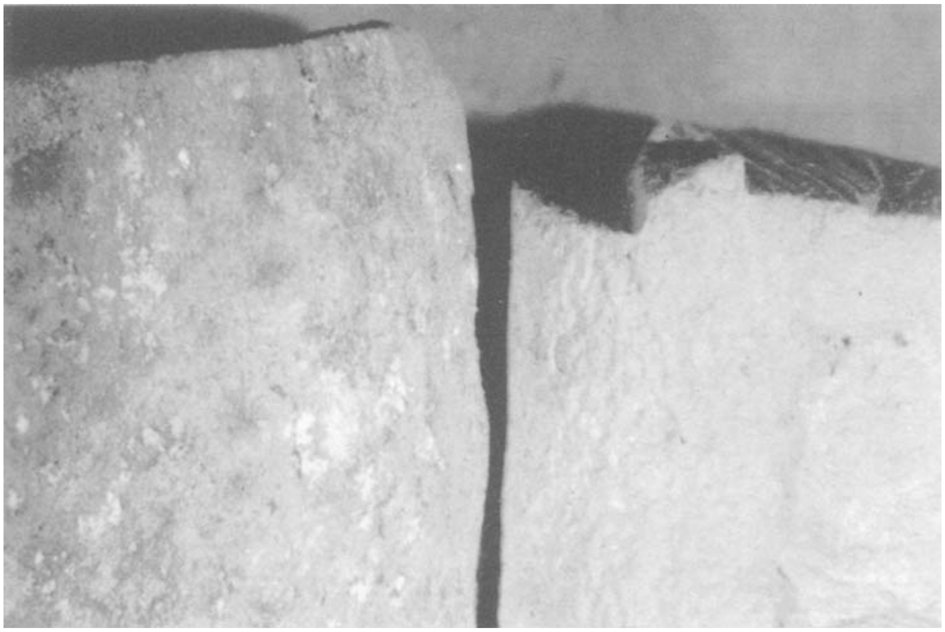


Figure 5. Two samples from the same original bangle fragment, stored in cups (8x magnification). The undesalinated control (left) shows white fluffy salts, while no changes are visible on the sample desalinated to 400μS/cm (right), after 4 years.

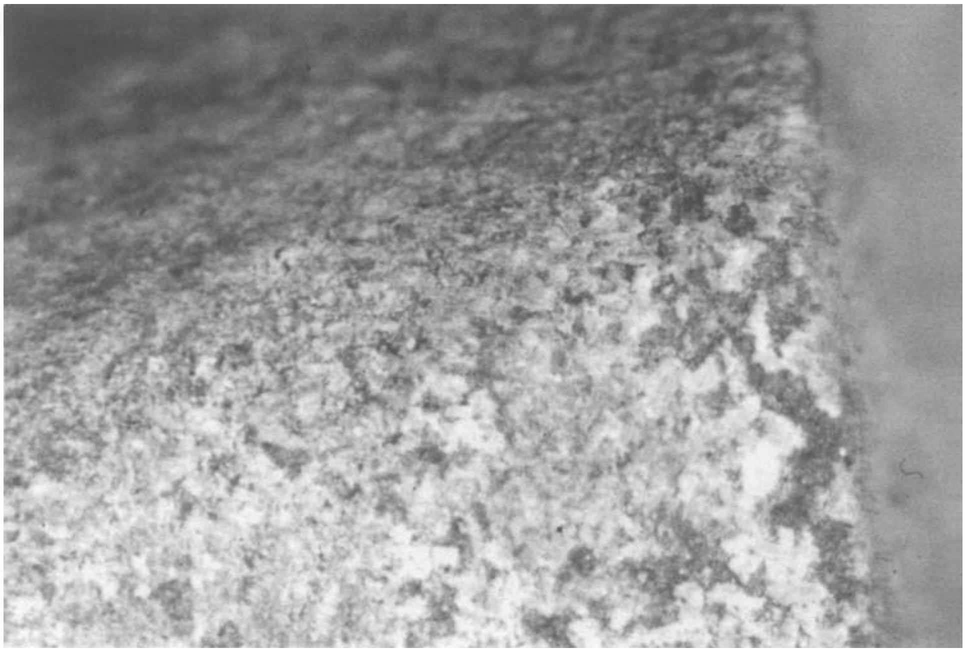


Figure 6. An undesalinated sample stored in a cup, after 4 years (20x magnification). A whitish crust has developed on the exterior surface, containing calcium sulfate dihydrate (gypsum) with some sodium chloride, as analyzed by XRD.

Figure 7. A sample desalinated to 400μS/cm, after 4 years (8x magnification). The cut surface exhibits fine reddish brown spots in the center and concentrated near outer edges.

Figure 8. Undesalinated terracotta figurine fragments, stored in a polyethylene bag. The fragment on the left manifests salts as reddish brown blotchy spots.

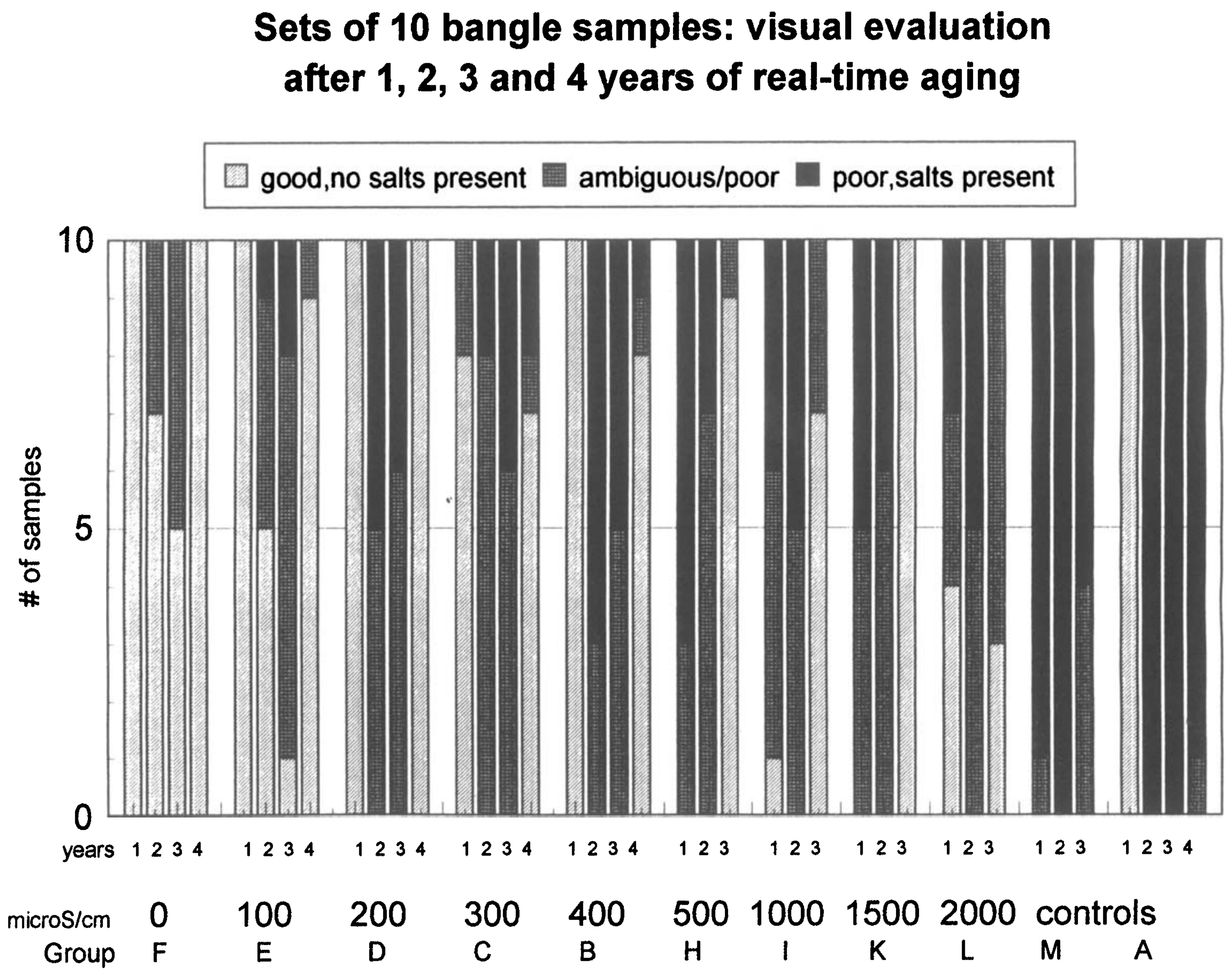


Figure 9. Real-time aging experiment. Visual evaluation of standard sets of bangle samples (10) from each group. Ratings for Groups A-F are from 1996 to 1999, and from 1997 to 1999 for Groups H-M.

TECHNICAL ANALYSES OF PAINTED INKA AND COLONIAL QEROS

Ellen J. Pearlstein, Emily Kaplan, Ellen Howe and Judith Levinson

1. Introduction

Wooden drinking vessels known as qeros have been used for the ritual consumption of maize beer in the Andean region for millennia, and are still used today for ceremonial purposes in traditional communities. The prevalence of Spanish motifs on highly decorated painted qeros places them firmly in the Colonial period, between the seventeenth-nineteenth centuries. Inka qeros, dating from the fifteenth-sixteenth century, are mostly unpainted but are decorated with incised geometric designs, which correspond with designs found on Inka textiles. Both Colonial and Inka qeros were carved in matched pairs, but few actual pairs are documented in American museums or private collections, having been separated through the process of the art market (figs. 1-2).

Carved and painted wooden qeros are widespread in American museum collections, but, like many museum objects, there is limited documentation about their provenance. The authors have access to a combined total of more than 150 qeros in their four museum collections, which form the corpus for this study. Many scholarly investigations have been made into the chronology, iconography, and historic and ethnographic contexts of qeros (note for example, Rowe, 1961, Cummins, 1988, and Flores, 1998), but significant questions about materials and techniques of Inka and Colonial qero production remain unanswered. In this paper, we describe the preliminary results of an ongoing collaborative study designed to characterize these materials and methods of manufacture. A second aim of our study is to examine what these technical choices might tell us about qero patronage, production, individual workshops, chronology, or the introduction of non-indigenous materials. Other authors who are currently studying qero technology include Ramos, et. al., 1999, and Rivery, et. al., 1998.

The authors worked in consultation with conservation scientists, primarily Richard Newman at the Museum of Fine Arts, Boston, and with tropical wood expert Regis Miller at the U.S. Forest Products Laboratory in Madison, Wisconsin. Curators in charge of Andean collections at each museum, and qero expert Thomas Cummins, an art historian at the University of Chicago, participated in the study by providing literary references and assisting with the interpretation of results.

Our results thus far indicate that wooden qeros are technically uniform products from the Inka through the Colonial periods, and that the carving style and method of paint application continue a pre-Hispanic tradition indigenous to the Andean region. In most qero studies, iconography has been the primary basis for dating: virtually all extant Inka period qeros display incised geometric motifs while Colonial period qeros are decorated with painted figural, floral, and faunal narrative motifs. We determined that while iconography became increasingly influenced by narrative European styles during the Colonial period, many of the materials and techniques used to create the qeros remained the same.

2. Description of project

The project to examine qero materials and technology has included visual analysis, identification of wood types, sampling for cross-sectional analysis, sampling for the identification of pigment and binder materials, and replication studies to assist us in understanding the paint application techniques.

Each of the more than 150 qeros in the four museum collections was surveyed and comprehensively documented with written descriptions, photographs, and drawings. For the documentation, each qero was examined with a binocular microscope and ultraviolet light source to evaluate the appearance of carving and paint application, and the state of preservation. Each examiner used the same survey form that we designed specifically for this project, so that uniform technical information was recorded for each cup (fig. 3). The completed survey form includes observations about the following characteristics: iconography, dimensions, shape, paint colors, appearance of paint application, appearance of carving and finishing methods, the presence or absence of possible maker's or owner's marks on the bases of the qeros, types of metal decorations, and types of repairs (indigenous and later). To compare paint colors on qeros in different museums, each color was matched to Munsell color standards from the Munsell Book of Colors using consistent lighting sources.

3. Visual Results

Visual examination of the qeros indicates that the forms were always carved in the longitudinal direction of the wood. We suspect the use of a compass to establish cup base diameters, or a turntable for the application of horizontal register lines, as there are shallow depressions in the center of the base of most qeros[1] (fig. 4). The painted decoration seems to have been planned by first incising shallow outlines with a sharp tool. Following the incising, paint was sometimes applied flush on top of the wood surface. More commonly, however, the paint was applied in cavities that were carved out in the wood to allow colors to be inlaid (fig. 5). Some qeros show a combination of these techniques. Colorants that retain some transparency have also been found applied on top of other more opaque color areas, or directly on the wood, creating a glaze like effect. Some motifs were carved to include cavities at two different depths in the wood: one opaque colorant would be inlaid into the lower cavity, and a second, more transparent colorant was inlaid over this in a larger, more shallow cavity. The motif would have two colors and increased depth, resulting from the transparent color passing directly over wood in one area and over the opaque pigment in an area of detail. Even though an inlay technique appears dominant, extremely fine details are also observed in some of the qero decoration.

4. Wood

Wood sampling from the generally well preserved qeros was deemed too intrusive to carry out on a routine basis. Instead, Regis Miller, a wood anatomist with a specialty in tropical woods, consulted at each of the four museums to examine features of the wood structure under magnification, without sampling. The coatings, wear, and paint on the qeros made it difficult for Miller to see wood features, but he placed the cups into preliminary groups based on physical characteristics such as density, weight, color, and grain.

Woods from qeros which date, based on iconography and, in rare instances, excavation records, to the Inka and Colonial periods were placed by Miller into different but overlapping wood categories. Conservators at two museums were able to remove samples for examination from a small number of selected Inka and colonial period qeros which have existing cracks and damages. Miller also examined Inka period wood specimens that author Kaplan had sampled from private collections in Peru. Miller concluded that all of the colonial woods observed and sampled appeared to be species of the genus Escallonia (common Andean names include chachacoma). The Inka period cups that were sampled were also Escallonia, but other Inka cups were visually assessed by Miller and were thought to be Alnus (alder), or Prosopis (mesquite). One Colonial qero at the American Museum of Natural History had been repaired with a section of another qero. Miller identified the wood of the Colonial qero as Escallonia, while the earlier repair fragment is of the Alnus species. The wood findings were surprising since palms, and especially chonta (the Quechua name for several species of palm), are most often cited in the literature as the wood used to manufacture qeros (Boussingault, 1985). Results from another recent study at the Museo de Americas in Madrid showed great similarity with our results (Carreras Rivery and Escalera, 1998). We intend to carry out more wood sampling where possible, as additional wood results may allow us to determine whether there is a chronological progression in the types of woods used for qeros. This may assist in dating qeros that are transitional.

Examination of the wood also revealed some interesting information about technique. While each of the qeros was carved in the longitudinal direction of the wood, they were not necessarily cut from the center of the tree as one might suspect. Instead, they were cut from an off-center part of the cross-section of a mature tree. At least one pair of qeros from the Metropolitan Museum of Art collection was actually cut from the same tree, one on top of the other, as the growth rings visible on both bases are super-imposable[2] (fig. 6).

5. Paint

The following results derive from the examination of the paint materials and techniques, which have received the most time and attention within the study. Visual observations about technique were followed by sampling select areas of the polychromy.

6. Sampling

During visual examination, potential paint samples sites were selected from the following: 1) microscopic areas selected for chemical analysis to identify the composition of the binder and/ or colorants and 2) cross-sectional areas that presented the opportunity to understand the pigment to binder ratio, the order of paint application, and the relationship between different layers. Cross-sections were sometimes stained with ultraviolet fluorescing stains to aid in the identification of separate layers.

Characterization and identification of the binders were carried out using Fourier-transform infrared (FAIR) microspectrometry followed by gas chromatography/ mass spectrometry (GC/MS). FAIR has been used first as a kind of screening method for organic materials, and portions of some of the larger samples from qeros were analyzed by GC/MS. Pigments were further identified by polarizing light microscopy and by electron microprobe spectroscopy.

6.1 Binder

We began our work on the paint medium by analyzing a botanically vouchered sample of a South American resin from the plant *Eleagia pastoensis* Mora. The exudate from this plant is known by the common name of mopa mopa. This resin had been suggested by other researchers as a possible paint medium used on Colonial Andean wood objects. The vouchered sample was obtained from the collection of the Colombian botanist Dr. Eduardo Mora Osejo through Jean Portell, a private conservator in New York. Since then we have been comparing the results of these analyses to those of the samples of the paint from Inka and Colonial period qeros in the four museum collections. To date, more than 150 samples have been analyzed by chemists at conservation research laboratories: primarily by Richard Newman, Conservation Scientist at the Boston Museum of Fine Arts, Boston, Massachusetts, and also by conservation scientist George Wheeler and staff at the Metropolitan Museum of Art, N.Y. We have obtained vouchered specimens from economic botany collections from other plant exudates, including balsam, Peruvian pepper tree resin, and copal, which would have been available for use as paint binders in the Andean region.

Our results show that the binding medium used to decorate Inka and Colonial qeros best matches the processed exudate of Egaegia pastoensis Mora. A semi-drying oil often appears mixed with the plant resin. None of our samples match the traditional European paint binders linseed oil or walnut oil, nor do they match any of the other native Andean exudates in the reference group. We have identified the composition of Inka period beads from Colombia to be mopa mopa resin[3], and have similarly found mopa mopa as the paint binder in a pair of excavated Inka qeros currently in a museum in Cuzco (Llanos, L. A. , 1936). This confirms a knowledge of the resin's existence and working properties prior to the Spanish conquest.

Documented botanical sources for mopa mopa are restricted to the montana of southwest Colombia in the region of Putumayo (Mora-Osejo, L. E., 1977). This area, in conjunction with neighboring northern Ecuador and including the Colombian city of Pasto, is thought to constitute the northernmost extension of the Inka empire (Salomon 1986). Seventeenth, eighteenth, and nineteenth century European naturalists who visited the city of Pasto described in detail the use of the plant in the production of an exquisite material most often called barniz de Pasto but also known as barniz, mopa mopa, mopa mopa de Pasto, barniz de Mocoa, and barniz de Condagua, which they found being used to decorate such things as wooden objects, leather, and gourds (Botina, 1990).

Barniz de Pasto is still produced by artisans in Pasto today. *Eleagia pastoensis* produces an enormous quantity of resin: the end buds on the branches of the trees are encased in resin. The raw material, comprising a large compressed cake of resin and plant parts, is hard and an opaque pale green in color. After repeated heating in water and manual manipulation, the mass softens and becomes malleable and elastic. This facilitates the removal of plant parts and other foreign matter by hand. When all of the impurities are removed, the mass has a putty-like texture. The cleaner it is, the more translucent and less green the resin. Powdered colorants are mixed into this elastic mass which is then pulled and stretched by two people to the thinnest possible sheet of uniform thickness. For modern folk and tourist art, barniz de Pasto is cut into shapes, either freehand or according to patterns, and then applied to a wood substrate (Friedemann, N. S., 1990). Today, some barnizidores ensure that the thin shapes of barniz de Pasto adhere to the wood substrate by first coating the wood with oil paint or a commercial adhesive, followed by placing under pressure. Sometimes a final coat of commercial varnish is applied.

6.2 Colorants

Though only a minority of Inka qeros are painted, the mineral pigments we identified on Inka qeros continued to be used in the Colonial period, when other colorants were added. Both mineral pigments and plant based pigments have been identified on the Colonial cups. The additions made to the palette in the later period includes pigments derived from mineral processing and others of organic origin such as browns, blues, and certain reds. Mixtures of pigments are also widespread in the Colonial period, increasing the range of colors.

An intense yellow colorant found on many qeros derives from orpiment, a sulfide of arsenic. This pigment appears both in mixtures and in varied concentrations to produce a number of yellows ranging from orange to tan. This platy, reflective pigment, identified as realgar and pararealgar, was also used in low concentrations in the medium resin where it appears golden and reflective. It should be noted that Colonial artists in the Andean region were using orpiment in imitation of gilding on paintings depicting Christian imagery (Tomkiewicz, 1995).

The most common pigment found on the qeros is a deep opaque red that has been identified as cinnabar, or a sulfide of mercury. Cinnabar has a long tradition of use as a pigment in the Americas. On the qeros, cinnabar is sometimes mixed with white to create a pink color. Several organic reds were also detected, but have not yet been fully identified. The fugitive nature of these organic colorants has resulted in a dull purple appearance on the exposed surface, with an intense red color only identified on the interior areas in cross-sections. Organic reds were noted as colorants in Peruvian paintings from the 17-19th c. in a previous study at the Brooklyn Museum of Art (Tomkiewicz, 1995).

White and cream colors, seen only on the Colonial and not on the Inka qeros, were mostly identified as lead white. Cerrusite, a neutral lead compound, is the form most commonly found. Hydro-cerrusite, a basic lead carbonate, was also identified, mixed with cerrusite in some cases. Both forms of lead white are likely to be products of Colonial industry as, to date, no references to pre-Hispanic lead white have been identified in the literature.

The blue-green, green, and yellow-green colorants fall into two broad categories. The first are those that contain indigo, alone or in combination with other pigments such as lead white and orpiment. When used alone, indigo often appears as green because of the tinting effect of the currently yellow binding medium. Colonial Peruvian canvas paintings make frequent use of indigo, either mixed with lead white (Seldes, M. et. al, 1999), or mixed with a yellow pigment to produce greens found in foliage (Tomkiewicz, 1995).

The greens in the second group all contain a pigment that is copper based. Some of them are formed from naturally occurring minerals such as brochantite and malachite, which were used in pre-Hispanic metallurgy. The others generally appear to be artificially manufactured copper salts such as verdigris. There is to our knowledge no documented instance of the use of verdigris as a pigment in pre-Hispanic America.

Earth pigments, *i.e.*, those derived from iron compounds, appear only rarely to form browns. Other complex mixtures of organic materials, as yet unidentified, were also used to create browns. Black pigments have consistently been found to be based on carbon.

7. Replication Experiments

The authors decided to try to replicate the production and application techniques for mopa mopa, based on published accounts, visual observations, analytical results from our corpus of qeros, and on modern craft practices. In our replication experiments, we started with fresh plant samples collected in Colombia by Ellen Howe, following the processing steps that she and others have observed in use by the Pasto barnizidores. Since our analysis has identified a semi-drying oil as well as mopa mopa in our samples from qeros, we have attempted to incorporate different oils into our mopa mopa. However, neither traditional nor contemporary barnizidores recognize this addition. We have added mineral pigments to our resin mixture and have worked it while warm by pressing the pigment resin mixtures into carved recesses in wood. Thus far in our replication experiments, we have found that the addition of oil produces samples which are very similar to qero decoration. When viewed in cross-section, the replication samples show a smooth, even mixture of pigment and resin, similar to that seen in qero cross-sections. For certain pigments such as lead white, the addition of oil was essential to the production of a smooth pigment resin mass. We have also been able to cut extremely finely detailed forms out of the pigment resin mass, which can be inlaid into larger color areas using a heated tool such as a spatula. Some of the fine details observed on qeros in our museums appear fluid and painterly, though our replication studies indicate that such fine details may also be pulled out like threads and then inlaid (figs.7-8).

It has been useful to learn about the modern technique of barniz de Pasto. However, it is clear that the application of paper-thin sheets of barniz de Pasto to wooden objects with smooth surfaces is not the same as the application of the processed and colored resin from Elaeagia pastoensis Mora used in qero inlay. First, the paint layers on the qeros are quite thick - several millimeters - much thicker than the paper-thin modern barniz de Pasto. Second, unlike the modern technique, there is no indication of a preliminary adhesive layer used in the production of qeros.

8. Conclusions

All of the investigative phases of this work are ongoing. Future work includes the creation of a relational database for all information collected. We hope this will aid us in comparing and grouping the results of analysis to determine the frequency and trends in qero decoration, and will increase our understanding of historical and technological events during the Colonial period. In addition, we are investigating other pre-Hispanic objects decorated with paints with plant exudate binders from the Andean region, in an effort to better understand the possible sources for the qero decoration techniques.

Our original sample group consisted of more than 150 unexcavated qeros in our four museum collections. We have sought, and continue to seek out, samples for analysis from excavated or well documented painted Peruvian and Colombian pre-Hispanic objects to try to determine the earliest use of the sophisticated mopa mopa technique. Thanks to the generosity of the UNSAAC Museo in Cuzco, Emily Kaplan was able to examine a pair of excavated Inka qeros with inlaid paint decoration and to take tiny samples necessary for analysis. Analysis of these samples indicated that they contain the diagnostic binder mopa mopa and pigments similar to those found on our museum qeros. Judging by these findings, the Inka period application technique appears to be similar to that of the Colonial period. The decoration on the qeros displays a technical sophistication that far surpasses what would be expected in a new or experimental technique. We are therefore anxious to understand why these materials and techniques, many of which were pre-Hispanic, experienced a florescence in the post-Inka period.

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Endnotes

1. Thanks to Lisa Bruno, Associate Objects Conservator at the Brooklyn Museum of Art for sharing this observation.

2. Metropolitan Museum of Art accession numbers 1994.35.22 and 1994.35.23.

3. Inka period beads found in an uncontrolled excavation of tombs in Miraflores, Colombia, have been identified in this study as mopa mopa resin. Other pre-Hispanic beads, purportedly also of mopa mopa, have been systematically excavated in the same region of Colombia, but the records of these findings are largely unpublished.

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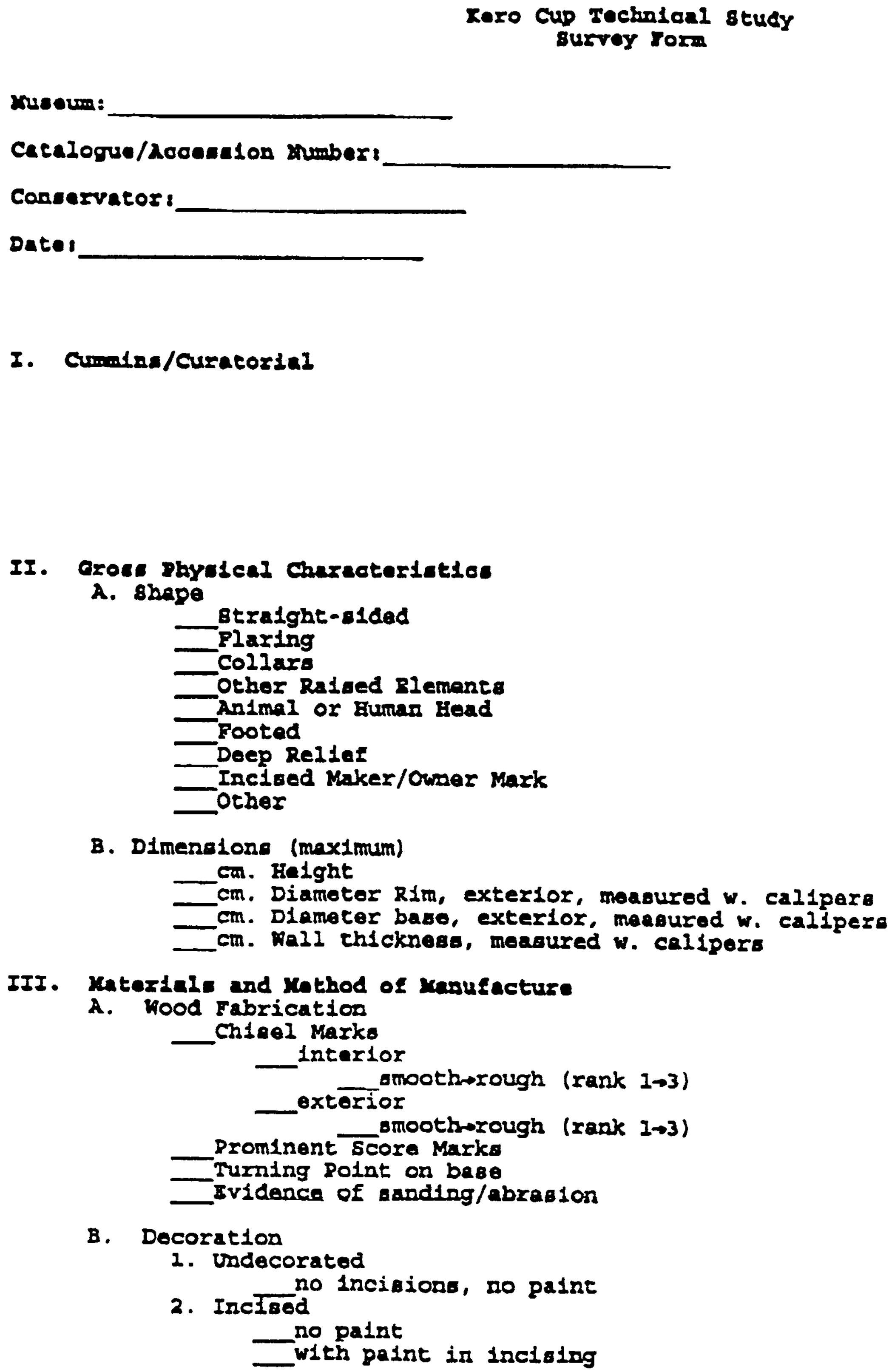
Figure 1. Pair of incised wood Inka qeros. Photo: Giannoni Succar, courtesy of Museo Inka, Universidad Nacional del Cuzco, Peru. After Flores et. al. 1998, p. 15.

Figure 2. Pair of carved and painted wood qeros, 18th c., Photo: Giannoni Succar, courtesy of Museo Inka, Universidad Nacional del Cuzco, Peru. After Flores et. al. 1998, p. 225.



Kero Cup Technical Study
Survey Form

Museum:________________________

Catalogue/Accession Number:____________________

Conservator:____________________

Date:________________________

I. Cummins/Curatorial

II. Gross Physical Characteristics
- **A. Shape**
  - ___Straight-sided
  - ___Flaring
  - ___Collars
  - ___Other Raised Elements
  - ___Animal or Human Head
  - ___Footed
  - ___Deep Relief
  - ___Incised Maker/Owner Mark
  - ___Other
- B. Dimensions (maximum)
  - ___cm. Height
  - ___cm. Diameter Rim, exterior, measured w. calipers
  - ___cm. Diameter base, exterior, measured w. calipers
  - ___cm. Wall thickness, measured w. calipers

III. Materials and Method of Manufacture
- A. Wood Fabrication
  - ___Chisel Marks
    - ___interior
      - ___smooth→rough (rank 1→3)
    - ___exterior
      - ___smooth→rough (rank 1→3)
  - ___Prominent Score Marks
  - ___Turning Point on base
  - ___Evidence of sanding/abrasion
- B. Decoration
  - 1. Undecorated
    - ___no incisions, no paint
  - 2. Incised
    - ___no paint
    - ___with paint in incising

Figure 3. Sample pages from the qero study survey form.

3. Coloring
  a) Bound opaque colors present (list all, by Munsell # range)
    ___ red
    ___ cream/white
    ___ light red orange
    ___ tan/yellow
    ___ yellow
    ___ peach
    ___ green
    ___ light yellow green
    ___ dark yellow green
    ___ light blue green
    ___ brown
    ___ light brown
    ___ dark brown
    ___ tan brown
    ___ black
    ___ other

  ___total number of bound colors present

  b) Application of bound colors
    ___ Surface (no inlay, assumed to be proud of surface)
    ___ Inlay

      ___ single layer
      ___ carved In
      ___ multiple layers
      ___ proud of surface
      ___ flush with surface
      ___ recessed

    ___ Overlay (particle rich)
      ___ single color
      ___ more than one color
    ___ glaze (particle lean paint over inlay), 1 color
      ___ more than one color of glaze

  c) Solubility of binder

  ___ water ___ethanol
  ___ acetone ___pet. benzine
  ___ tol/xyl ___other

  d) craqueleure
    ___ regular "network"
    ___ none
    ___ other

  e) ___ presence of bubbles

C. Varnish
  1. Appearance in visible light
    ___ not visible
    ___ multiple applications
    ___ Relatively Translucent
    ___ Black
    ___ dark brown
    ___Pigmented
    ___Unusual Build-Up in Craquelure
    ___Other

2. Appearance under UV Illumination
   - ___ Unvarnished
   - ___ varnished before incising
   - ___ Varnished
     - ___Exterior
       - ___ full
       - ___ partial
     - ___Interior
       - ___full
       - ___partial

3. Color of varnish on unpainted wood under UV Illumination (standards TBD)
   - ___green ___yellow
   - ___orange ___white
   - ___other

4. Solubility of varnish
   - ___ water ___ethanol
   - ___ acetone ___pet. benzine
   - ___ tol/xyl ___other

D. Metallic Decoration

1. Recessed Studs
   - a. Location
     - ___Rim
     - ___Panel
     - ___Raised Elements
   - b. Identification of Metal
     - ___Pb ___Ag
     - ___Sn ___Alloy

2. Raised Studs
   - a. Location
     - ___Rim
     - ___Panel
     - ___Raised Elements
   - b. Identification of Metal
     - ___Pb ___Ag
     - ___Sn ___Alloy

3. Other Applied Metallic Elements
   - a. Location
     - ___Rim
     - ___Panel
     - ___Raised Elements
   - b. Identification of Metal
     - ___Pb ___Ag
     - ___Sn ___Other
   - c. Method of Join
     - ___Nailed
     - ___Adhered
     - ___Crimped

VII. Condition

A. Structural
- ___ Cracks
- ___ Losses

B. Surface
1. Surface coloring (bound colors, not inlay)
___Unstable
___Loss
__Minor
__Moderate
__Severe

2. Inlay (bound colors)
___Unstable
___Loss
__Minor
__Moderate
__Severe

3. Varnish
c) Degree of Intact Condition of Film
Interior
___generally intact
___worn
___removed
__abraded
__solubilized

Exterior
___generally intact
___worn
___removed
__abraded
__solubilized

4. Metal decoration
___ losses
___ tarnish
___ corrosion
___ wear

5. Accretions
__Fatty Bloom
__Crystalline Bloom
__Repair Associated
__White Drips
__Burial Dirt
__Other

VIII. Post-Manufacture Treatment

A. Presumed, No Longer Extant, Native Repair
1. Holes
__Filled
__Unfilled
__Covered

B. Native Structural Repairs Associated with Cracks

1. Applied Adhesive
a. Solubility
___ water
___ acetone
___ tol/xyl
___ethanol
___pet. benzine
___other

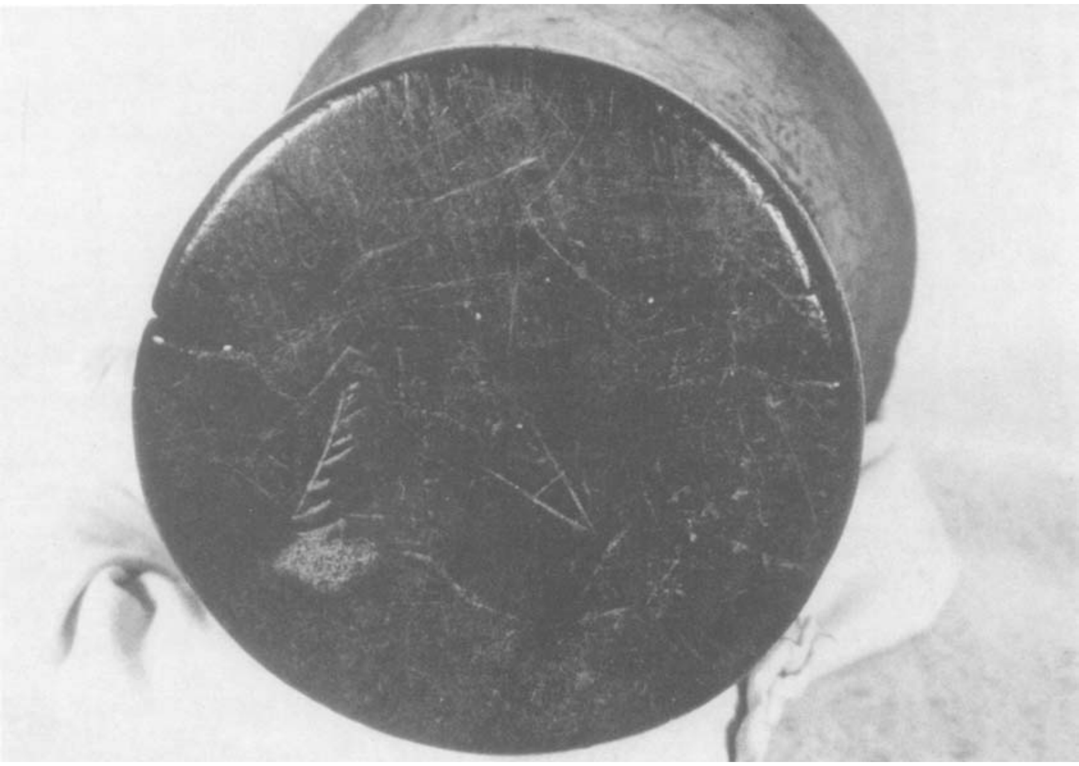


Figure 4. Base of a wooden qero showing central depression, and "feather" and "A" shaped incisings. Brooklyn Museum of Art accession # 36.357.

Figure 5. Colonial period qero showing incised and carved areas with color inlay. Brooklyn Museum of Art accession # 36.356.

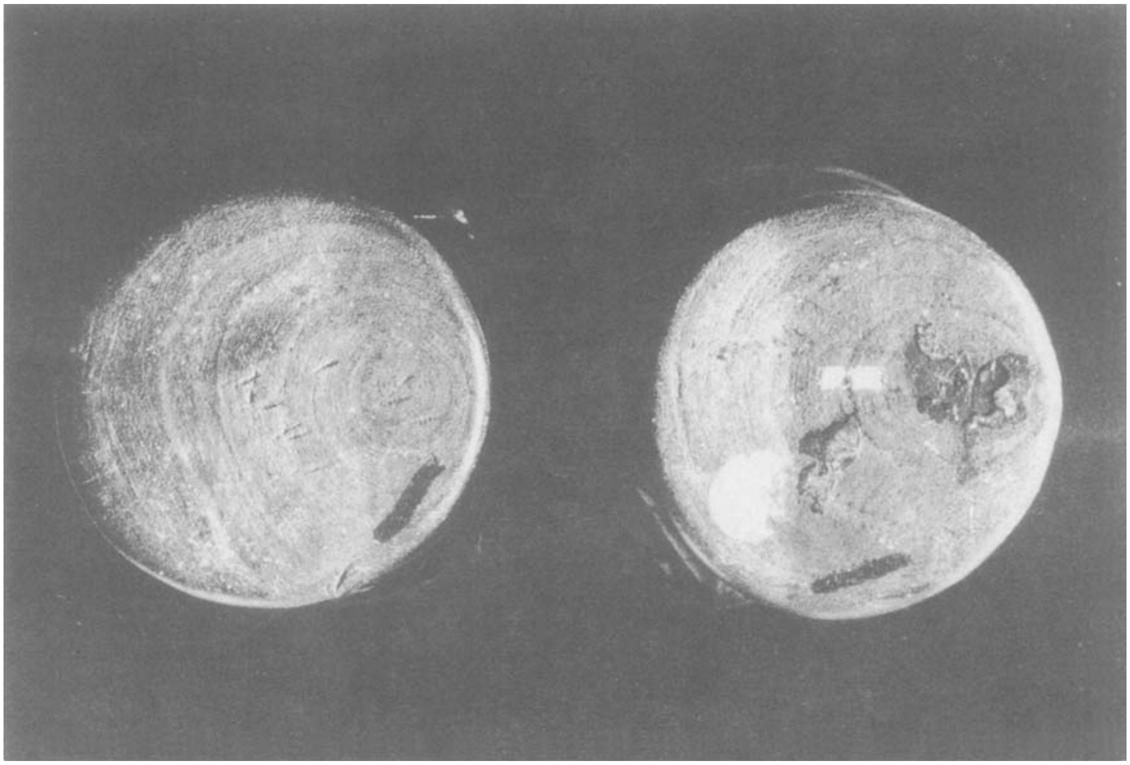


Figure 6. Bases of a pair of qeros made from the same tree. Metropolitan Museum of Art acc# 1994.35.22 and 1994.35.23.

Figure 7. Replication work showing processed, pigmented mopa mopa inlaid in a channel carved in wood. Threads of contrasting colored mopa mopa have then been inlaid in a second step.

Figure 8. Detail of a qero with fine inlays. National Museum of the American Indian, accession #163605.

AFTER THE FIRE AT THE CHURCH OF LA COMPAÑIA DE JESUS, QUITO, ECUADOR

Constance Stromberg

Abstract

La Compañía de Jesús is a high style Baroque church built between 1605 and 1767. Its interior is covered with ornately carved polychrome or gilded decoration and mural paintings. Located in Quito's historic city center, it has been under restoration since 1992. In January 1996, just as the conservation of the altarpiece of San Francisco Xavier was near completion, solvent fumes caught fire when an overloaded electrical outlet exploded. The fire affected an estimated 10% of the church, including more than 50% of the altarpiece, a portion of which was irretrievably lost. The main cupola was damaged, as were the four life-size relief figures of the evangelists just below. Numerous ethical and practical questions arose concerning what could be preserved and what was lost. Areas of the altarpiece considered totally lost, without form, or unstable were replaced and other pieces were conserved and remounted. As of September 1999, decisions have not been made concerning whether to repaint and regild burned areas.

The Quito school of art and conservation in the historic city are reviewed, as well as factors that may have contributed to the occurrence of the fire in the church. Several conservation problems and treatments undertaken in the church before and after the fire, along with the investigation and use of alternative resin/solvent combinations for consolidation of the burned wood are discussed. Conclusions are drawn from the resin investigation and treatment of some of the burned sculptures.

1. Introduction

Quito, Ecuador is located at 9,300 feet, in the Andes Mountains of South America. It is now roughly divided between colonial Quito and the modern city to the north, built after 1945. Much of old Quito has been left standing and was declared a World Heritage Site by UNESCO in 1978 (Afshar 1994). Spanish conquistadores moving north from Peru founded Quito in 1534, where the indigenous people had been conquered 60 years earlier by the Incas. The European conquerors built churches and buildings on the foundations of the Incan buildings they ruined (Keleman 1957).

The Quito School of Art was founded in the middle of the 16th century at the church of San Francisco de Quito. Local and Peruvian artisans were trained in the European techniques of carpentry, sculpture, and painting by Flemish, Spanish and Italian priests and artisans. This was the first of many churches in colonial Quito built and decorated by indigenous artists (Vargas 1982). In the 16th century, European images and designs were copied for religious images, with technical and stylistic developments added throughout the 17th and 18th centuries (Escudero de Teran 1992). Quito School churches are highly ornamented, within a framework of Renaissance and Baroque building plans. Facades are carved in stone and the floorplan is in the form of a cross, with at least one cupola, a main altar and side altarpieces to various saints (Donoso 1983). Two of the best known and most sumptuously decorated churches are La Compañía de Jesús (fig. 1) and San Francisco de Quito (fig. 2).

2. Conservation in the Municipality of Quito

While they do not have great financial resources, Quiteños take pride in their heritage. The Municipality of Quito funds conservation of its historic buildings through the Fondo de Salvamento, which oversees projects contracted out to private conservation companies. Each church is also responsible for the care of its historic structures. However, during the conservation at La Compañía, the priests were mostly concerned with continuing religious practices in the church without interruptions from the ongoing work. The devoted also expect the images they worship to glorify the church, and not necessarily to show the patina of time.

2.1 La Compañía de Jesús

Begun in 1605 and finished in 1767, during the high Baroque style, La Compañía de Jesús is modeled after Gesú in Rome, the mother church of the Jesuits. Layer upon layer of decoration was added to this huge structure over 15 decades (Keleman 1957 and Vargas 1982). Locally quarried volcanic andesite (*andesitico valsaltico*) was used for the stone façade and other walls (fig.3). Interior walls are mainly decorated with painted stucco, molded plaster designs and woodwork. The central cupola is plaster over pumice stone blocks, and walls supporting altarpieces are brick.

La Compañía is said to contain seven tons of gold leaf in its approximately 70 meter long by 25 meter high interior. There is a main altar, a pulpit, a high central nave and eight floor-to-ceiling altarpieces (*retablos*) in vaults along the sides containing paintings and polychrome and gilded wood balconies, balustrades, columns and sculptures (fig. 4). Four high relief, life-size polychrome evangelist figures are just below the central cupola, and there is a smaller cupola over the main altar. Mural paintings of the 12 archangels, lunettes of 12 cardinals, 37 polychrome wood winged cherub heads, and molded and painted plasterwork adorn the central cupola (fig. 5).

2.1.1 Techniques of Polychrome Sculpture

Polychrome sculpture techniques from the Quito school have been well-documented (Escudero de Teran 1992, De Vuyst and Beltran 1992) and are summarized here for reference to treatment problems of sculptures in the church. Technical information and methods of construction for individual pieces are given here when known by the author. Although analytical testing was at times subcontracted out at La Compañía to address specific conservation issues, such as analysis of certain paint layer cross-sections and stone samples, wood was often only identified visually.

Quito School figures began with whole logs or blocks of wood glued together with animal glue, then carved and finished. Commonly used woods included cedar (*Cedrela odorata*) and alder (*Alnus accuminatta*). Knots and imperfections were sealed with animal glue, and then the wood was gessoed with a mixture of animal glue and calcium carbonate or calcium sulfate, after which more fine finishing was carried out. Flesh (*encarne*) and other areas were painted in oil, animal glue or egg tempera colors, sometimes with wax added. Pigments included lead white, vermilion, malachite, azurite, bone black, verdigris and earth colors (De Vuyst and Beltran 1992).

Not all polychromy on the sculptures in La Compañía were gessoed before painting. In the cupola black paint on the cherubs' hair was applied directly on the wood, but the *encarne* of the faces has gesso layers beneath, that vary in composition from fine to coarse. Cross-sections taken from the face of a cherub in the cupola after the fire showed two layers of calcium carbonate gesso separated by a layer of animal glue. Identification of burned *encarne* paint was inconclusive.

Areas to be water or mordant gilded were coated with Armenian bole then gilded with gold or silver leaf and tooled by the gilder (Portell 1992). Water gilding often had transparent oil glazes. Elaborately patterned garments were detailed in color on the gold or silver leaf base, in a painting over metal technique called *estofado* or quilting. The *escrafiato* technique continues by scribing into the paint layer to reveal a pattern in the metal leaf below and is illustrated by the garments of the evangelist figures (fig. 6). Added after the 17th century, *estofado a la chinesca* employed colored varnishes over silver gilt areas to give them the appearance of gold. In the 18th century, garments were often made using *tela encolada*, plaster covered cloth that was gilded and painted.

2.1.2 Conservation at La Compañía de Jesús

Dampness, soluble salts, fungal problems and insect infestations are continuous problems in Quito buildings due to heavy periods of rain and large daily temperature gradients (Gomez-Moral 1994). Pollution and human occupation also cause problems in Quito churches. The most recent major earthquake hit Quito in 1987 and damaged the central transept and cupola and the south wall of La Compañía de Jesús.

La Compañía has been undergoing its current restoration since 1992. Contractors have worked on the interior and exterior of the central cupola to try to correct problems caused by dampness and soluble salts in the building fabric and decoration. Extensive work was also done on polychrome and gilded wood, mural paintings and painted plasterwork in the main altar, the retablo of San Francisco Xavier, and in other areas of the church. However, it is not possible to present complete information here about treatment methods and materials used as many different contractors were involved and not all documentation was accessible. The work included: fumigation with pentachlorophenol; consolidation of worm eaten wood with Acryloid B72 in lacquer thinner; replacement of insect damaged wood; surface cleaning and repair of polychrome sculptures; and removal of overpaint layers on some important sculptures.

In the cupola, the combination of calcium sulfate gesso, porous volcanic stone and dampness has caused worsening problems over time, requiring at least five courses of conservation treatment in the past century. This was exacerbated in 1993, when an unsupervised crew improperly replaced mortar between glazed ceramic tiles on the exterior, causing further ingress of water. That mortar was replaced again with a water-repellent silicone mortar in 1997.

The group that directs and funds the current project is comprised of the Municipality's Fondo de Salvamento, the Instituto de Patrimonio Cultural and the Jesuit church. This team plans and oversees all conservation decisions and work specifications. Private restoration firms carry out the work with approximately 30 workers between them, many of whom also study in the conservation training program at the Technical University of Quito. Although the philosophy of the participants is to adhere to accepted conservation procedures, including the use of reversible materials and documentation, there is pressure to work quickly and minimize costs.

3. The Fire

In January 1996, as the conservation of the San Francisco Xavier altarpiece neared completion, solvent fumes caught fire when an overloaded electrical outlet exploded. Fire swept up from the altarpiece into the cupola, also damaging the main altar and the arch of the transept. The fire department responded rapidly, so that only approximately 10% of the entire church was affected. Fortunately, many of the sculptures from the San Francisco Xavier *retablo* had not been reinstalled. Only one of its four columns was severely burned, but they all suffered water damage and loss of water gilding and gesso layers when the fire was extinguished (fig. 8). More than 50% of the altar sustained damage, including about 35% that was irretrievably lost. The *encarne* layers on several images in the main altar became blistered and distorted.

The fire was drawn into the cupola when the scaffolding boards under the four relief figures of the evangelists just below the cupola ignited. These figures were severely damaged by the intense heat given off by the burning boards. Paint and ground layers were burned away from the heads, hands and feet, and their wood surfaces were charred, but the sculptural form and the gold leafed and painted garments remained (fig. 6 and 7). Mural paintings on plaster in the cupola sustained fire and water damage. After the fire was extinguished, further problems with soluble salt crystallization occurred as the water soaked cupola dried out toward the interior of the church. Two of the archangel oil paintings on linen were lost (fig 9). The cherubs and other wooden elements burned in varying degrees of severity depending on the path of the fire as it swept through the cupola towards the windows at the top (fig. 12).

After the terrible reality of this disaster registered with those working on this national treasure, numerous ethical and practical questions arose concerning what was considered lost, what could be preserved and the methods to be chosen for compensation of losses. The decision was made to recarve in cedar what was determined to be totally lost, without form, or unstable. Other pieces were kept, such as carved and gilded decorative wooden panels burned at the back but with well defined surface detail (fig. 10). Images and decorative areas that were partially burned but with some gilding or paint layers intact, and very important pieces, such as the four evangelists have been conserved. However, some questions may never be answered, including: the extent and morphology of damage in individual pieces; and the value of consolidating carbonized wood when surface layers and an unknown quantity of substrate were lost. Air circulation in the church remains inadequate; however, explosion proof outlets and upgraded wiring are now in place.

4. Conservation After the Fire

Bubbled paint was treated on some of the main altar images soon after the fire (fig. 11). Blisters were poulticed with cotton soaked in dilute animal glue, which was also injected under the bubbles. A heated spatula was used to reform blisters after facing with tissue.

Conservation of the interior of the cupola after the fire began with the rebuilding of the huge work platform at its base. From the platform we could see and feel tiny particles of spalling paint and plaster raining down on us, as the crystallizing salts pushed off surfaces of the mural paintings and painted plaster. These exfoliating surfaces had to be immediately stabilized. Conservation of the mural paintings and plaster moldings in the cupola are outside the scope of this article (see Rogers 1980 and Schwartzbaum 1985). It is important to note here that the crystallizing salt problem had to be mitigated by facing and consolidating the spalling mural paintings before soot removal, making it much more difficult to remove soot after consolidation. Other problems included: removal of degraded PVA consolidant (Borden Polico 2153) used on murals and painted decoration before the fire; removal of soot and burned Acryloid B72 surface coating; drying and stabilization of the cupola walls; and treatment of burned polychrome sculptures (fig. 12).

4.1 Investigation of Consolidants for Burned and Worm-eaten Wood

My involvement in the project began in May 1996, with one of the contractor companies called Trateggio. They asked me to investigate consolidants, communicate with experts about the treatment of burned wood and do empirical tests on samples of burned and insect damaged wood. This investigation was undertaken so that Trateggio could recommend treatment options to the project supervisors, for the burned red cedar *retablo* elements, and the cherubs and evangelists. We decided to compare Acryloid B72 in various solvent combinations and Butvar B98 in alcohol, following a literature search and personal communication with researchers at the Forest Products

Laboratory and the Canadian Conservation Institute (Barclay and Grattan 1997, Schniewind 1997).

The stability and use of Acryloid B72 in conservation is well documented (Carlson and Schniewind 1980). Butvar B98 is manufactured by Monsanto for lamination of car windshields (Monsanto 1989). It is resistant to heat and light aging and has also been tested and used in conservation to consolidate degraded wood for more than 20 years (Grattan, 1980, Schniewind and Kronkwright 1984, Wang and Schniewind 1985, Barclay 1987 and 1990). Although it does have a slightly yellowish cast, this is not a problem when charred wood is the material to be consolidated.

Our testing had two primary goals:

- To find a safer resin/solvent combination to use in the uncontrolled church environment.
- To determine if Butvar B98 consolidation could give sufficient strength and penetration, and add less weight to the cherub and evangelist figures that were mounted at acute angles.

Consolidant penetration through fragile char layers, down to the interface with sound wood was necessary. Figure 13 shows a cross-section of one of the burned red cedar samples, illustrating the thin boundary between burned and sound wood as well as cross-grain fissures that commonly form in the weak char layer (Zicherman 1981). Worm-eaten red cedar samples were included to observe resin penetration more readily and to look for treatment alternatives for the ongoing problem of insect damage in the church.

Acryloid B72 in lacquer thinner is the resin of choice in most developing countries, due to its stability, availability and low cost. However, the flammability, toxicity and retention of lacquer thinner fumes in poorly ventilated areas cannot be overemphasized. Consolidation tests were done with Acryloid B72 in acetone and ethanol to offer a safer solvent option if Acryloid B72 was chosen over Butvar B98. However, acetone is a controlled substance and difficult to obtain in Ecuador, due to its use in cocaine production, so lacquer thinner generally is used instead.

4.1.1 Empirical Tests

Consolidant was applied by syringe to surfaces initially pre-wetted with ethanol. Samples were kept in closed containers for one day between applications to slow evaporation and improve resin penetration. Resin was applied 16 times to all samples (see charts for different concentrations) and surfaces remained glossy by the 14th application on many of the burned ones. Because of uneven absorption by the randomly burned and worm-eaten wood, resin quantities varied between 10-20 ml. for each application. Immersion was not feasible due to dissolution of carbonized wood in all solvents. Impregnation under low pressure would have increased penetration but was ruled out due to the unknown depth of carbonization and fragility of protruding design elements.

4.1.2 Consolidation Test Results

Although these tests were done on site with uncontrollable variables, rudimentary methodology, and discarded sections of burned and worm-eaten wood, the results offer practical treatment information. One drawback of Butvar B98 illustrated well during the tests was its high viscosity. Burned samples consolidated with 10-15% B98 showed resin buildup on surfaces after only few applications, so the tests were modified. Penetration improved markedly by diluting the B98 resin to a 3% solution for the first five or six applications, then increasing the concentration to 7.5%.

Charts 1 and 2 show the different resin concentrations and the weight gains of samples consolidated with Butvar B98 and Acryloid B72 in burned and worm-eaten cedar (fig 14). Samples with Acryloid B72 in thinner gained more weight in both cases, partly because of better resin penetration, due to lower viscosity and slower solvent evaporation. The worm-eaten samples gained between 40 and 110% of their weight due to their tunneled structures. Burned samples became from 3.3 to 7.4% heavier, since the carbonization only penetrates about 3-6 millimeters and there is nonporous, sound wood beneath.

Consolidation with both resins in different solvent combinations appeared to have penetrated through the char layer in the samples, to the interface with sound wood, when each piece was sliced through to assess depth of penetration. However, results were inconclusive in the burned samples, due to the presence of Acryloid B72 consolidant applied just before the fire. In our empirical strength measurements the Butvar B98 samples were harder and more resistant to thumbnail scratches than the Acryloid B72 samples. After seeing the higher strength and lighter weight of the Butvar B98, best illustrated by handling the sponge-like worm-eaten samples, the team was convinced it was the better option for treatment of sculptures mounted at acute angles in the church. However, Acryloid B72 appears to achieve better penetration than Butvar B98 and may be suitable for burned wood consolidation in other situations.

4.2 Dismounting and Consolidation of the Cherubs in the Cupola

We began the first phase of the conservation of the burned wood with the removal and consolidation of 37 cherub heads from the cupola. Due to the rapidly deteriorating condition of the cupola, it was not possible to do a complete technical study of the cherubs before treatment. After removal of loose carbonized material, the cherubs were faced with tissue and gauze applied with dilute polyvinyl alcohol, then dismounted by cutting the four nails holding them to the cupola wall.

The cherubs were removed for consolidation because of their acute angle of attachment to the cupola and because of dampness trapped in the wall behind them. After their removal, deep holes were drilled into the pumice stone where they had been removed. Drying of the cupola wall was aided by inserting Pellon sleeves containing silica gel into these holes, which were periodically taken out and oven dried to remove moisture from the silica gel.

The facing was mechanically removed from the cherubs in the workshop, after dampening with cotton poultices. Loose charred surfaces were removed mechanically, down to the gesso layer. Discolored but un-carbonized paint was not removed. Cherubs were consolidated with nine to 18 applications of 3% Butvar in isopropanol or ethanol (depending on availability), applied by brush and syringe. Between applications of consolidant the cherubs were kept in sealed containers, to improve penetration by slowing evaporation of the solvent. After consolidation, 10% Butvar in alcohol was injected into cracks and large fissures were filled with Grilonit epoxy bulked with glass microballoons. Chunks of carbonized wood from points of hair or noses, which had detached due to shrinkage during evaporation of the alcohol, were readhered with Acryloid B72 adhesive.

The highest row of 12 cherubs, called *estipites*, were more badly damaged due to previous insect attack (fig. 15). Fire penetrated these figures more easily, through the network of exit holes left by the borers. Since they were vertically attached, we could partially consolidate them in situ, with eight to ten applications of 3% Butvar B98 in alcohol, before their removal. They were consolidated further in the workshop with approximately ten applications of 10% Butvar B98 in alcohol. Overpaint was mechanically removed from the wings, revealing gilded scrollwork. Unfortunately, I had to leave Ecuador in June 1997, before the project was completed.

4.3 Epilogue: The Evangelists and the San Francisco Xavier Retablo

In April 1998 I was able to return and review some of the work done on the burned wood since I had left. Consolidation, cleaning and some fills were completed on the cherubs. The evangelists were surface cleaned, partially consolidated, faced, and dismounted, as was done with the cherubs. This time the challenge was greater due to their size, acute angle and attachment height. Also, the fragile estofado gold and painted layer on the garments was barely supported by the burned wood beneath. Enormous spikes holding the figures to wooden anchors embedded in the wall were cut from the back to dismount them (fig. 16).

Conservation of the San Francisco Xavier altarpiece was also completed. The infrastructure of the heavily burned midsection was rebuilt to support conserved and recarved panels, which were remounted after treatment. Soot was removed from gold leafed carved panels with turpentine. Butvar B98 in alcohol was used to consolidate salvageable burned sections, with the addition of pinholes made down to normal substrate. This facilitated penetration and insured a stronger bond between the carbonized and undamaged wood beneath. For gap filling and gesso materials, PVA emulsion mixed with glass microballoons was used, and epoxy bulked with microballoons was used to fill large losses.

5. Conclusions

After empirical testing, Butvar B98 in alcohol was chosen to consolidate charred wood on sculptures and decorative elements from burned areas of the church of La Compañía de Jesús. This treatment provided a safer method of conservation in an uncontrolled environment. It has also introduced a proven conservation material to conservators working in Ecuador, where access to new materials is often limited. Other widely used conservation materials, such as silicone rubber and glass microballoons also were introduced during this project. Acryloid B72 in thinner also continued to be used for conservation of wood in the church, in a safer manner than before the fire. Further tests for the treatment of burned polychromed and gilded wood should be undertaken by a conservation facility equipped to carry out more controlled procedures, in order to obtain measurable results on the use of consolidants for burned wooden sculpture.

The part of La Compañía that was effected by the 1996 fire now waits in limbo between conservation of damaged sections, and restoration of those areas that would integrate them into the resplendent interior. Decisions concerning the level of restoration that will be carried out will be made by a large committee composed of many voices. If the religious community prevails, an extensive repainting of burned areas will probably take place.

Acknowledgements

Being part of the conservation team at La Compañía was an invaluable experience. I would especially like to thank Manuel Jimenez and Ramiro Pozo of Trateggio, who were interested in learning about new materials, techniques and conservation literature. Although it was impossible to convince them to stop using turpentine or thinner, they were receptive to testing and using materials new to them, such as Butvar or resins bulked with glass microballoons. They were patient with my Spanish and generously shared their knowledge of the Quito School of Art.

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Sources of Materials

Acryloid B72: Rohm and Haas Company, Philadelphia, PA 19105, USA.

Butvar B98: Monsanto Plastics & Resin Co., 800 N. Lindburgh Blvd., St. Louis, MO 63166, USA.

3M Glass Bubbles (Type: K1): 3M Structural Products Department, 220-7E 3M Center, St. Paul, MN 55144

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Figure 1. Main altar of the church of La Compañía de Jesús.

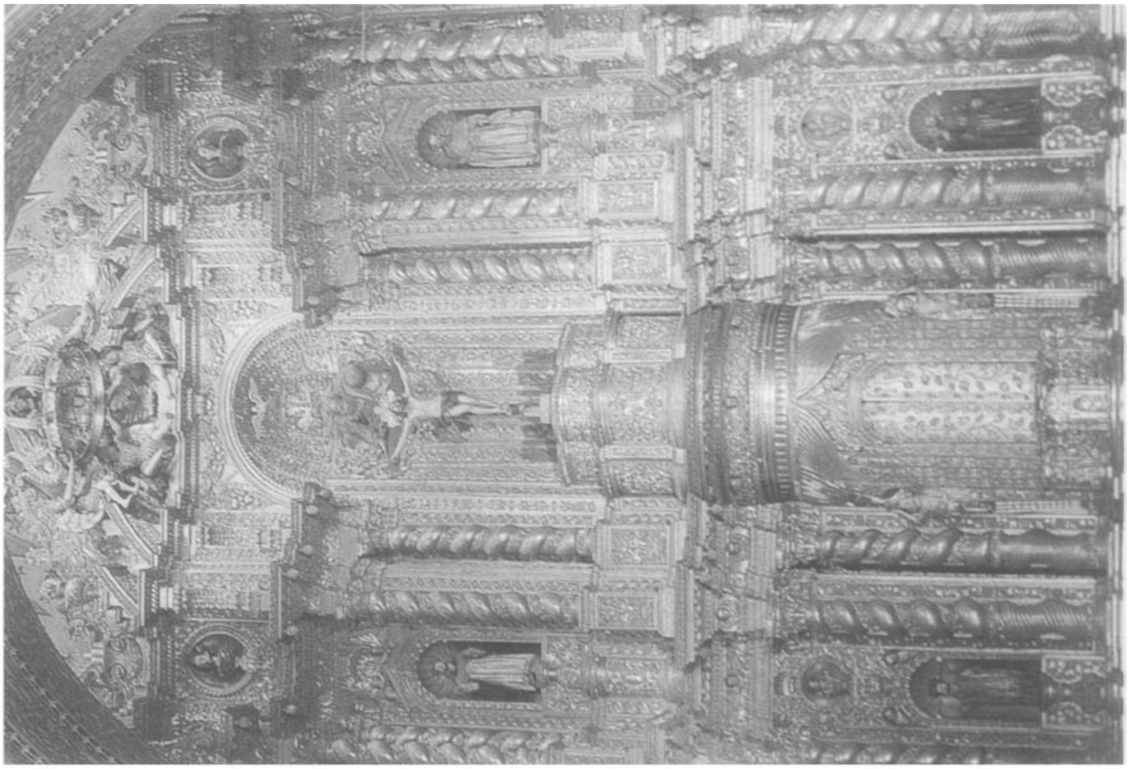


Figure 2. Main altar of the church of San Francisco de Quito.

Figure 3. Stone façade of La Compañía de Jesús.

Figure 4. San Francisco Xavier altarpiece before the fire.

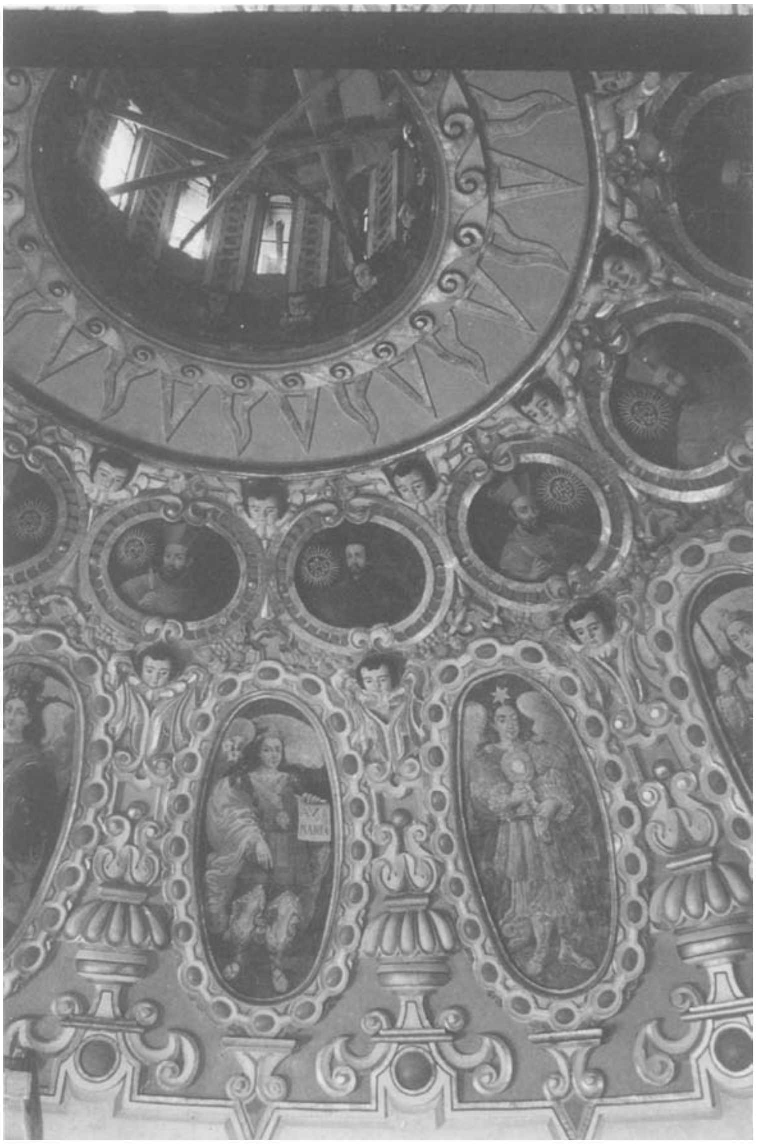
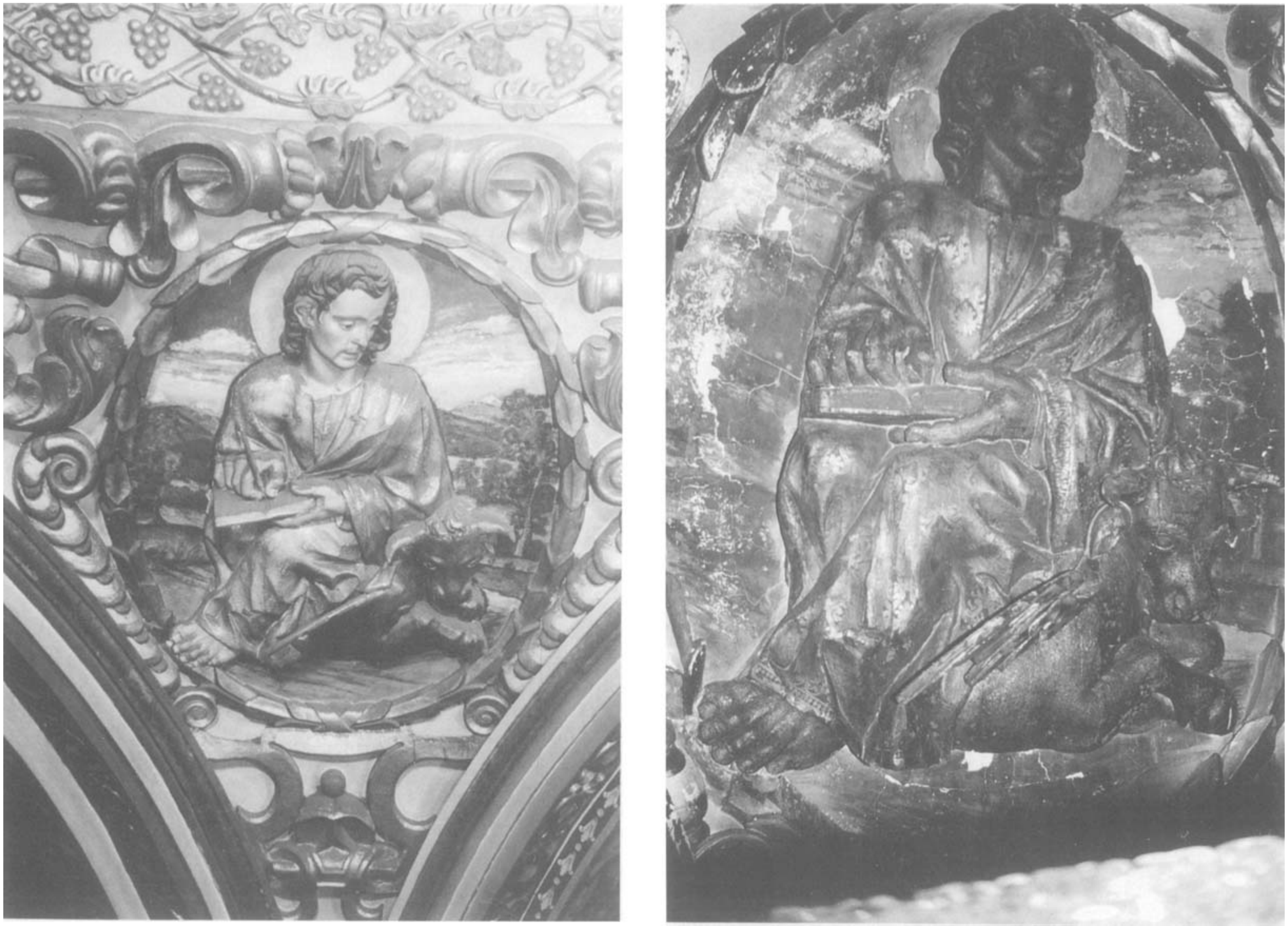


Figure 5. Mural paintings, cherub heads and plasterwork, central cupola, La Compañía de Jesús.



Figures 6 and 7. High relief life-size figure of the Evangelist San Lucas, before the fire on the left and after the fire on the right.

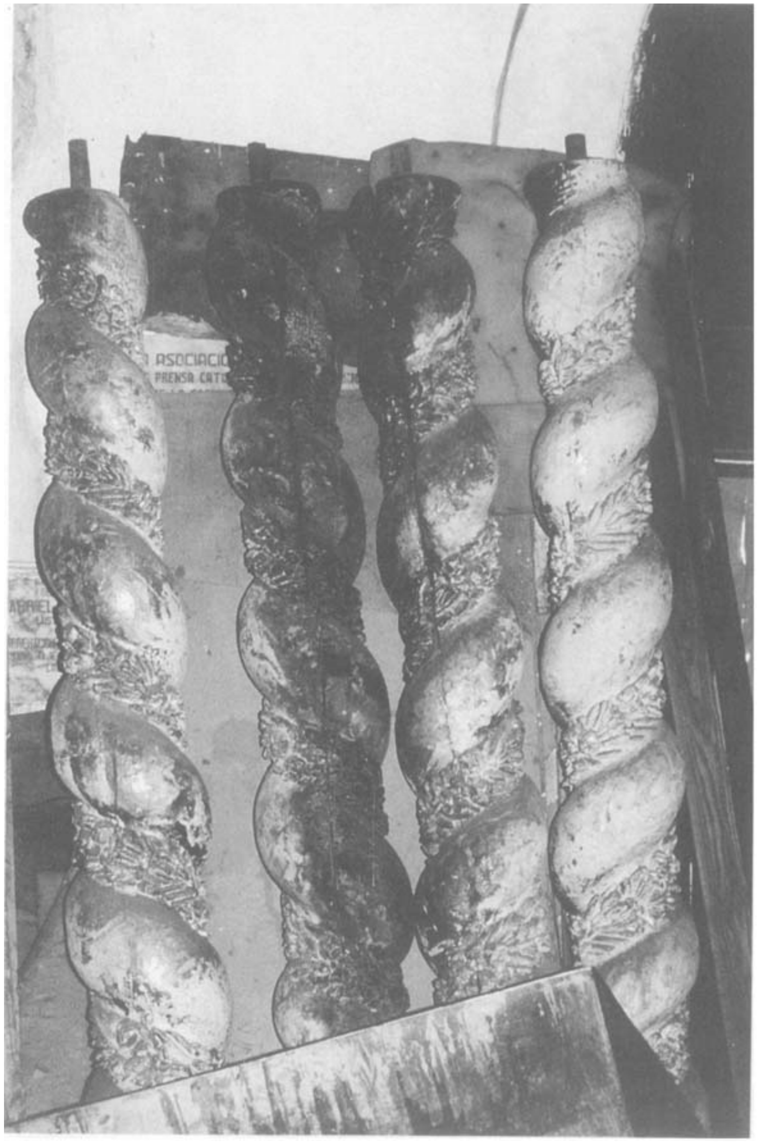


Figure 8. The four columns from the San Francisco Xavier altarpiece, removed after the fire.

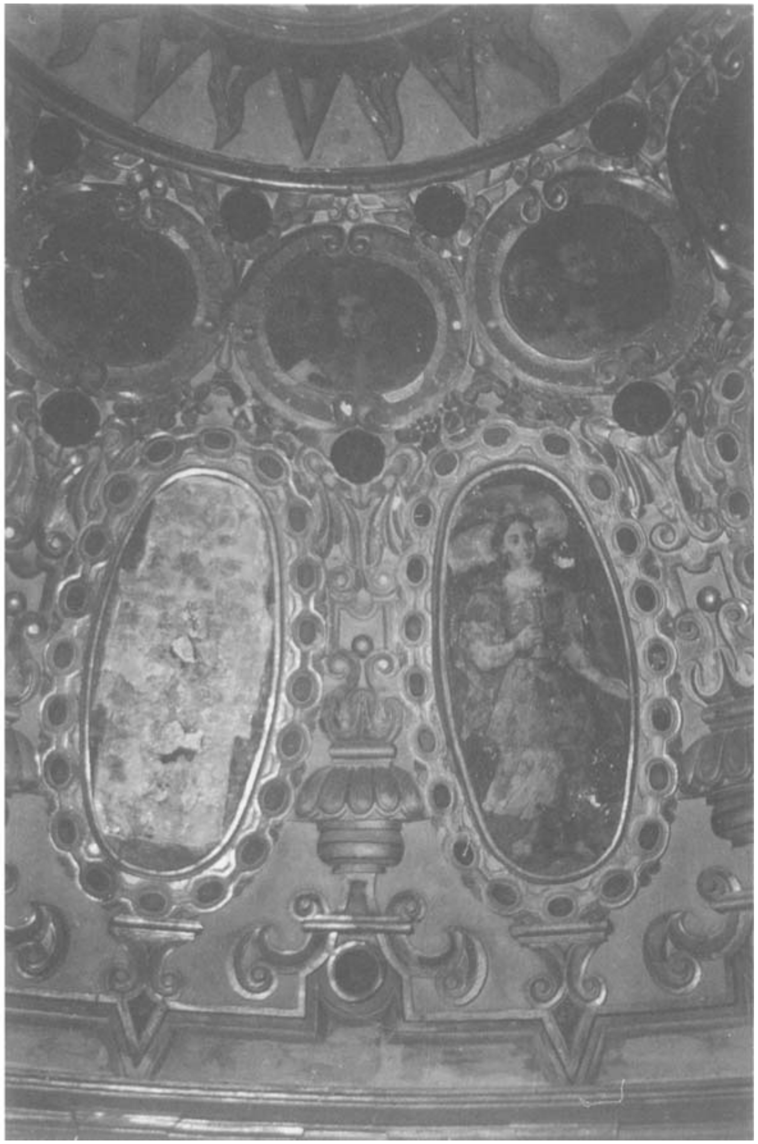


Figure 9. Burned cherub heads and lost painting on linen in the central cupula, after the fire.

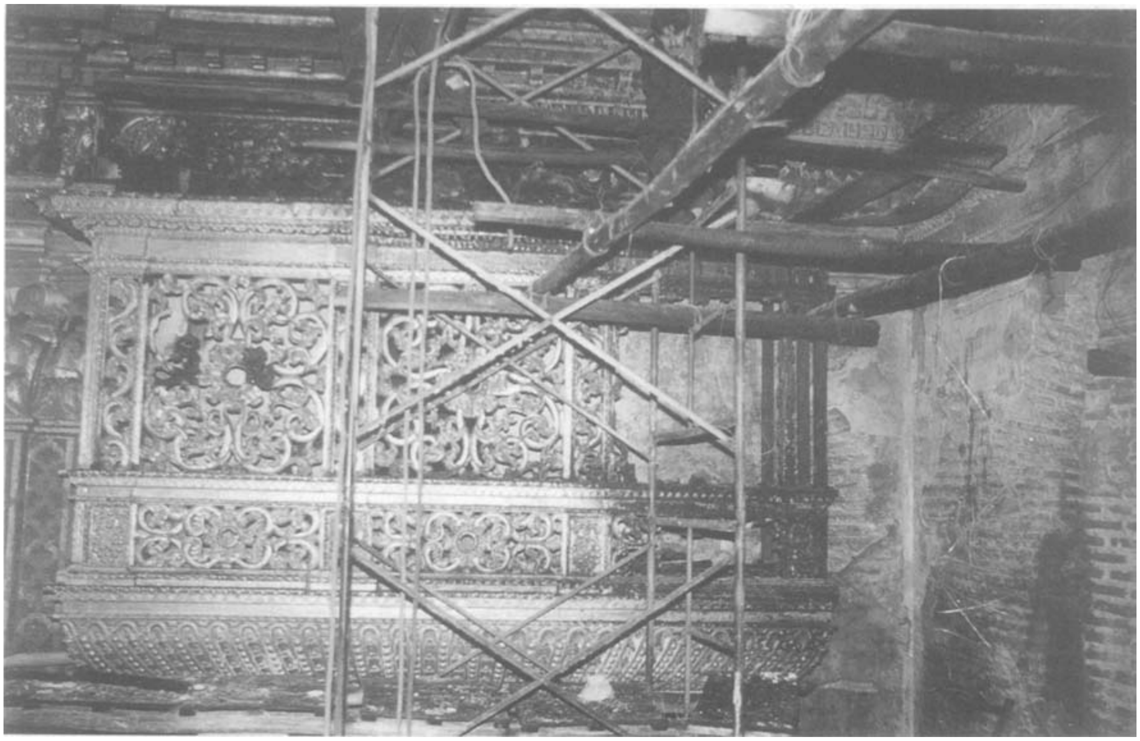


Figure 10. Partially burned gilded panels in the San Francisco Xavier altarpiece.

Figure 11. Blistered encarne on polychromed figure of an angel in the main altar.

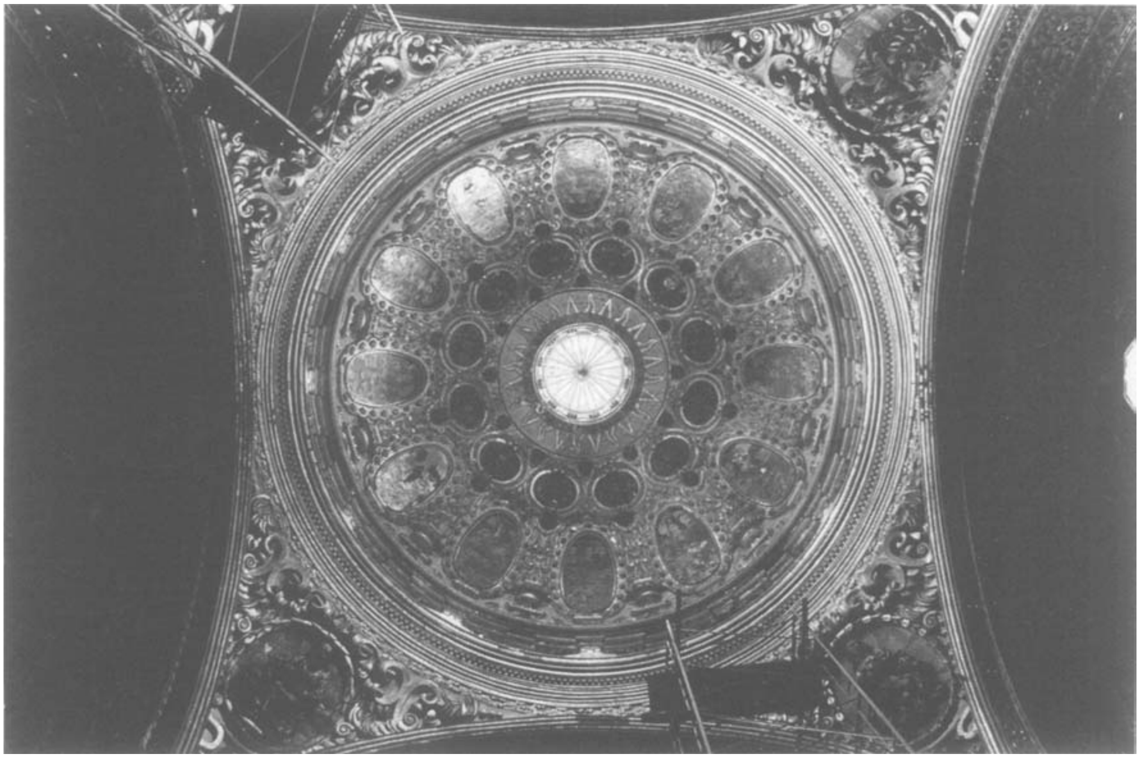


Figure 12. Central cupola, evangelist figures and scaffolding, seen from the ground after the fire.

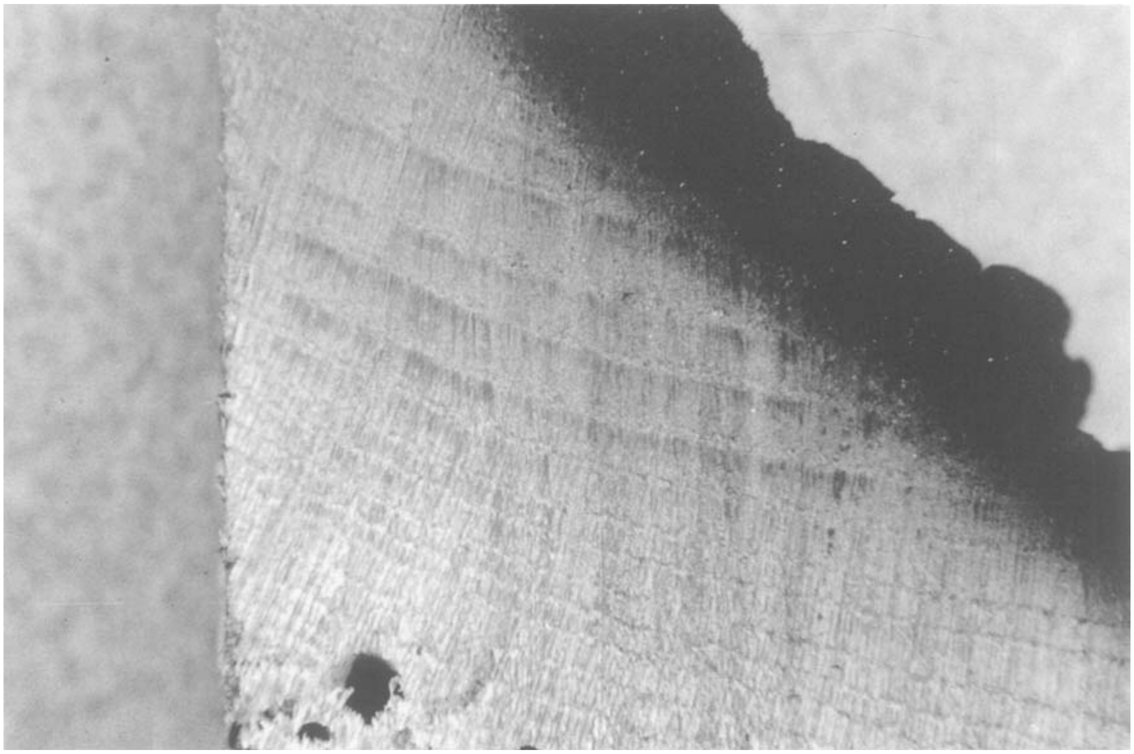


Figure 13. Cross section of a cedar sample showing the border between the char and sound wood.

CHART 1
Worm-Eaten Cedar Consolidated Samples

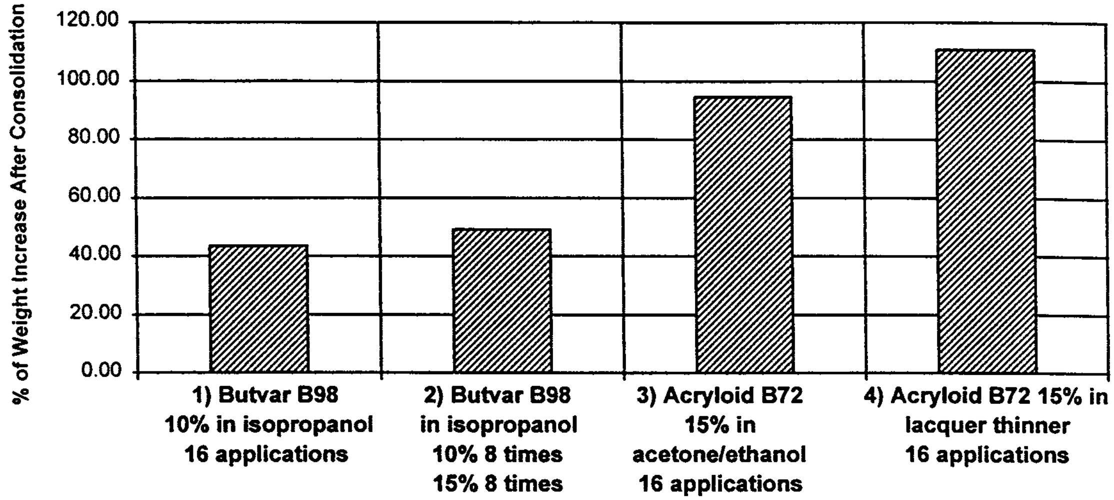


CHART 2
Burned Cedar Consolidated Samples

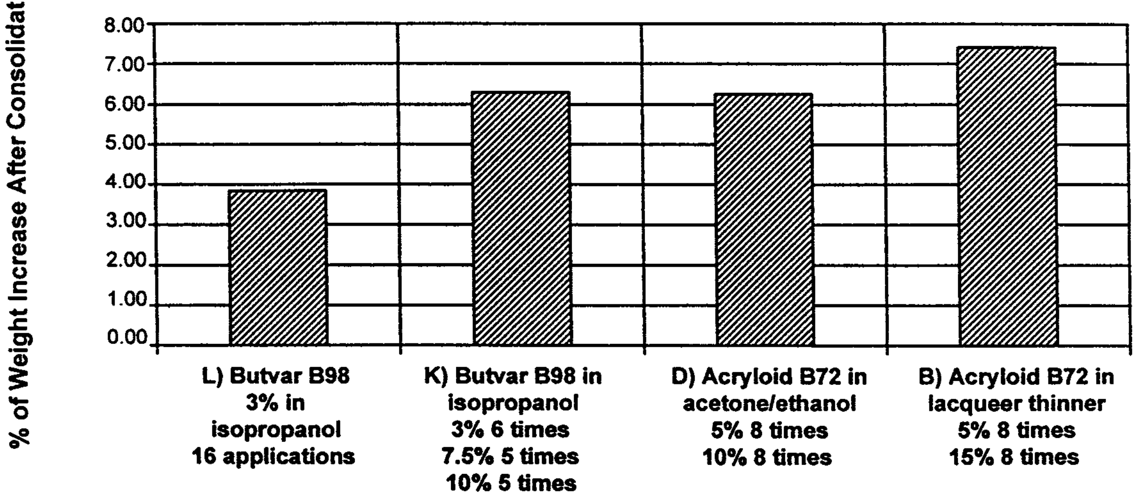


Figure 14. Charts 1 and 2 show the difference in weight gain between samples consolidated with Acryloid B72 and Butvar B98.

Figure 15. One of the estipites at the highest level, in the linterna above the cupola after the fire.

Figure 16. Dismounting of an Evangelist figure after partial cleaning, consolidation and facing.