Fig. 1. The Ghiberti's Paradise Doors on the east side of the Florence Baptistery; historical photography about 1900

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The Gilded Bronze Paradise Doors by Ghiberti in the Florence Baptistery

Scientific Investigation and Problems of Restoration

Introduction

Towards the end of the 1970's the conservation of the first two gilded bronze panels of the Paradise Doors of the Florentine Baptistery was preceded by one of the most extensive and complete diagnostic campaigns ever carried out on a bronze artefact.

The so-called Gate of Paradise (Fig.1) is the third and last door to have been executed for the Florentine Baptistery. Of exceptionally high craftsmanship, it was executed by Lorenzo Ghiberti between 1429-1452. Each wing contains five gilded bronze panels, approximately 90 x 90 cm in size, inserted within a bronze framework cast in one piece. The gilding was achieved with the amalgam technique. The panels depict scenes from the Old Testament. A perimetrically modelled frame surrounds them, also in gilded bronze, made up of 24 separate pieces. Panels and frame pieces were directly mounted into prepared door slots.

In short, the Paradise Doors are composed of:

two bronze wings,

10 (5 + 5) gilded bronze panels,

a total of 48 gilded bronze frame pieces (12 + 12 niches and 12 + 12 tondi).

It is also clearly a work of structural complexity where the artist has skilfully fused both a deep expression, which had a significant impact within the architectural context of the Baptistery, and highly refined and sophisticated detail (Ghiberti was an expert goldsmith). The modelling reveals a finish of very high quality even under microscopic magnification.

Immediately after World War II (when the Doors were removed to safety), an important restoration was undertaken between 1946 and 1948 by Bruno Bearzi. He carried out the cleaning of the Doors with rather drastic means (which were, unfortunately, used at that time). The grey-black-greenish incrustations which almost completely obscured the gilding, indeed its very existence had been virtually forgotten, were first removed with concentrated solutions of sodium hydroxide followed by nitric acid.

It is likely that these treatments further compromised the condition of the Doors, which already at that time were suffering from severe pollution damage.

During the great flood of 1966 which struck Florence, the rapid advance of water led to the detachment of six of the ten Door panels, causing them to fall to the ground. Consequently, even further damage, this time of a mechanical nature, was inflicted on the Doors. The detached panels were reattached to the doors with nails applied from behind the framework, resulting in perforation of the latter.

In 1979, on Umberto Baldini's initiative, the current director of the Opificio delle Pietre Dure of Florence, and under the responsibility of Loretta Dolcini, a new conservation campaign was begun. The Doors appeared to be covered again with the same type of incrustations which Bearzi had previously removed, and which had re-formed in the short span of only 30 years. At this moment, the above mentioned scientific investigation began, coordinated by the Scientific Laboratory of the Opificio, directed by myself together with Arcangelo Moles.

While the Laboratory was investigating conditions of degradation and researching an efficient cleaning method for the removal of contaminants but at the same time respectful of the original materials in their precarious state, researchers from the University of Florence as well as other research institutes carried out a series of complex studies related to the physical and historical aspects of the monument. The object of study was the panel depicting scenes from "The life of Joseph", the first to be conserved. The following investigations were undertaken:

- study of the technique of execution,
- gammagraphy for the study of fusion bubbles within the alloy,
- analysis of alloys (Table 1),
- a photogrammetric relief of the front and back with calculations of thicknesses,
- thermographic investigation for the study of thermal behaviour,
- double-exposure holography again for the study of thermal behaviour.

This systematic investigation not only brought to light a series of aspects relevant to the object, but helped to stimulate improvement of many investigative techniques which had previously only been sporadically employed in the study of monuments.

	sample N.3	sample N.5	sample N.6	sample N.7	sample N.9B
Ag	0.16	0.15	0.14	0.14	0.12
Sb	0.80	0.93	0.82	0.68	0.66
Fe	0.29	0.40	0.43	0.42	0.46
Ni	0.17	0.23	0.22	0.21	0.22
Pb	3.32	1.44	1.32	1.27	1.01
Zn	2.19	1.02	1.11	1.21	1.17
Sn	2.38	3.08	2.84	2.48	2.28
Cu	87.6	90.8	90.5	90.8	91.1

Table 1. Elemental analysis of bronze alloys in five samples taken from different points on the "St. Joseph" panel. The alloy in sample no. 3, taken from a small re-melted figure, is different from the others

Condition Survey

Relevant to a precise study of the condition of the work of art and determination of the individual processes which threaten its integrity, the following findings emerged from the investigation. The gilding was (and still is today), undoubtedly, the most threatened part of the object.

It represents one of the most expressive features of the artefact which gives it its very precious characteristics.

The amalgam gilding was very thin, approximately 5 μm thick on average, and its loss in a few areas in certain panels could be intuitively predicted. Indeed, as a result of the surface being largely obscured by dark grey-greenish incrustations, as mentioned above, it was not an easy task to gain a precise idea of the condition of the gilding. This, however, became much clearer after the first cleaning tests, which revealed the presence of micro-flaking of the gold, on average 0,5-1,5 mm in diameter and homogeneously distributed throughout all the panels (Colour Plate III.3). These manifestations were the first to be investigated.

By making a tiny opening with the point of a scalpel in a few of the small blisters (Colour Plate III.1, 2), it was possible to observe under the microscope the presence of greenish-blue compounds on the interior, most likely consisting of copper hydroxy salts. Samples were then taken and analysed by means of I. R. Spectrometry revealing the presence of hydroxy-sulphates and, more precisely, Brochantite and Antlerite.

Further in-depth and very detailed analysis of this phenomenon was later undertaken with the Electronic Microprobe and Auger Spectroscopy (Fig. 2).

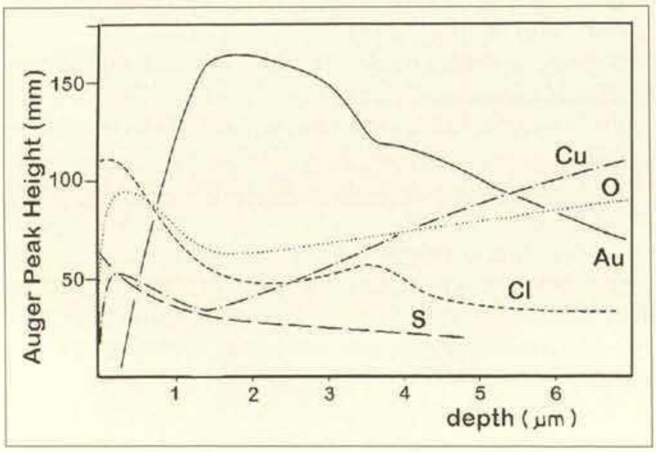


Fig. 2. Distribution of the elements in relation to depth from the surface, obtained by means of Auger Spectrometric analysis on the section of a gilded fragment

The formation of blisters is of galvanic origin, and certainly the case at the outset, which was progressively aggravated by the advent of industrial pollution and as a result of previous treatments with nitric acid.

Copper in the bronze alloy begins to oxidate on contact with the probably porous gold. Subsequently, dielectric substances (gypsum, cupric hydroxy salts) gradually accumulate between the two metals, accelerating the galvanic processes (Colour Plate III.4). The first corrosive action, in the form of pitting, which almost always occurs in bronzes, is due to chlorides: in the first place cuprous (Nantokite), then cupric (soluble chlorides, Atacamite, Paratacamite). Whereas chlorides corrode bronze provoking micro-craters in minuscule points beneath the gold, sulphates evolve from the latter, which are more voluminous and their crystallization pressure deforms and locally uplifts the gold film, creating blisters. The process continues until the gold micro-fragment detaches itself and is lost. The newly liberated salts migrate, spread and crystallize at the surface of the gilding where they meet and interact with the deposited products, in the first instance, with gypsum and then with carbonic and silicate particles. Gradually a discontinuous hard grey-greenish crust is formed in which gypsum acts as the main tenacious binder, the hydroxy salts, as secondary binders while carbon and silicates are embedded as particulate inclusions. The typical characteristics of colour and sheen of the gilding are lost. The surface increasingly resembles that of non-gilded bronze overlaid with disrupted patina-crusts which have originated from individual blisters.

This was the condition and appearance at the beginning of the 1980's when the first two panels (two of the six which had become detached during the flood) were brought to our laboratories for diagnostic investigation and then conservation. It must be pointed out that cross-section examination revealed an already uniform loss of direct gold/bronze contact in all of the locations sampled. Indeed, even in areas adjacent to the blisters, intervening corrosion compounds between the gold and bronze were always present, in the best of cases, oxides, otherwise oxides mixed with salts. In other words, this layer of oxides and salts constitutes the adhesive bed itself of the gold, a delicate and precarious condition.

Conservation Methodology

The fairly unstable physical condition of the gilding prevented the use of any mechanical method for the removal of patinas and crusts. We should not forget, however, that the latter not only severely altered the object's aesthetic appearance, but furthermore posed a direct threat to the conservation of the gilding itself due to its composition. For both these reasons, the incrustations should be removed.

Table 2 lists the principle alteration compounds identified by XR Diffraction and IR Spectrometry. As is shown in the table, in addition to inert insoluble particles, with an obscuring effect, such as carbon (clearly visible in the cross-sections), silicate particles etc., high percentages of gypsum, hydroxy sulphates, hydroxy chlorides and hydroxy nitrates are present. The latter are generally infrequent in outdoor bronzes. Their presence in this particular object may be explained by the previously mentioned treatment with nitric acid.

Gypsum	$CaSO_4.2H_2O$	predominant
quartz	SiO_2	elevated amount
feldspars	silicates	
tetrahydrate calcium nitrate	$Ca(NO_3)_2.4H_2O$	
antlerite	$Cu_3(OH)_2SO_4$	
copper hydroxy nitrate	$Cu_2(OH)_3NO_3$	
paratacamite	$Cu_2(OH)_3Cl$	

Table 2. Principal mineral contaminants identified with FT-IR and XRD on the surface of the "St. Joseph" panel

The diagnostic investigation reached the following conclusions:

1. the removal of only deposits on the surface would have fulfilled the aesthetic needs without, however, completely satisfying conservation requirements;
2. cleaning could only be undertaken by chemical and not mechanical means;
3. it was necessary to decontaminate selectively, where possible, even at the gold/bronze interface, where unstable (partially soluble) and, therefore, dangerous substances were present,

whereas the insoluble and, therefore, stable oxides – the actual support bed for the gilding – should be safeguarded.

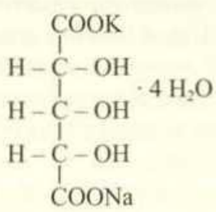
It was not easy to satisfy these requirements, which necessitated finding very selective reagents, capable of discriminating between oxides and hydroxy salts. These should be applied in solution and preferably by immersion of the object, so as to enable their diffusion through natural micro-openings even in internal parts below the gilding.

The complexing agents appeared the most suitable products which satisfied the above needs. These reagents in aqueous solution can sequester ions (generally cations) from salts, increasing their solubilisation.

complexing agent + cation-anion (salt)
→ cation-complex + anion

As to the properties of the complexing agent, the stability constant of the complexes needed to be higher than the solubility product of the hydroxy salts to be eliminated but inferior to that of the oxides to be conserved. The selective action was thus assured.

Following a specific experimental kinetic study, a suitable complexing agent was found in "Rochelle Salt", sodium potassium tartrate, an already well known agent in the field of bronze conservation, but normally employed only in a strong alkaline aqueous solution. EDTA and other more commonly employed agents, which were considerably less selective, were, however, inappropriate.



Rochelle Salt

Rochelle Salt in a concentrated aqueous solution (approximately 25% in water) has a neutral pH (7) and is, therefore, neither an acidic nor basic reagent, simply a neutral sequestrant capable of complexing both calcium (thus strongly increasing gypsum solubility) and copper (thus favouring the solubilisation of the hydroxy salts). On the contrary, it is completely ineffective on copper oxides, both on the very insoluble black monoxide (Tenorite) and on the insoluble red dioxide (Cuprite) (Table 3).

Although the action of the reagent is slow, given the neutral pH, it fulfils certain requirements. There is sufficient time for permeation of all the pores and micro-cavities of the surface. The laboratory experiments necessarily had to be followed up by preliminary tests on the object.

The first controls were carried out on the central door panel of the right wing depicting scenes from "The life of St. Joseph". Horizontally laid, a natural cavity within the modelling was exploited by delimiting it with plasticine to form a small tank (approximately 100 cm^2), in which the first cleaning test was carried out (contact time ca. 2.5 hours – a saturated solution of Rochelle salt in distilled water – room temperature – periodic movement of the liquid without touching the surface). The result was most surprising and very effective. All the surface incrustations had completely disappeared and the brilliancy of the gilding had been perfectly recuperated. At the same time, the oxides were preserved (indeed, in *lacunae* of the gilding directly ex-

	time (seconds)	bronze alloy	Cu_2O	CuO
Rochelle Salt	20 40 90 180	<0.1 <0.1 <0.1 <0.1	0.3 0.4 0.3 0.4	<0.1 <0.1 <0.1 <0.1
alkaline Rochelle Salt	20 40 90 180	<0.1 <0.1 <0.1 <0.1	0.4 0.4 0.4 0.4	<0.1 <0.1 <0.1 <0.1
tri – sodium EDTA	20 40 90 180	<0.1 <0.1 <0.1 <0.1	2.0 5.0 12.5 23.0	<0.1 <0.1 <0.1 0.1
"mixed bed" ion - exchange resins	20 40 90 180	<0.1 <0.1 <0.1 <0.1	9.2 14.4 19.4 19.8	0.6 0.6 1.0 1.3

Table 3. Percentage values of bronze alloy and copper oxides dissolved by the reagent solutions

posed to the action of the reagent the typical brownish-red tone of Cuprite was preserved). The small bath area was subsequently enlarged by a few centimeters and the operation identically repeated. Contact time of the Rochelle salt in the new zone was 2.5 hours, whereas it was doubled to 5 hours in the old area (2.5 and 2.5 hours).

No change was observed in the central area (5 hours) in relation to the preceding appearance (2.5 hours). Similarly, no difference was registered between the two adjacent zones subjected to different contact times (2.5 and 5 hours). This provided firm evidence that the neutral Rochelle Salt solution behaves as an intrinsically selective reagent, whose action, in the context of the panel, does not depend on contact time but only on the solvent properties themselves. An appropriate reagent for the conservation treatment was thus available.

A full methodology was then planned with different treatments on the panel primarily within a glass tank (preliminary cleaning of the back (non gilded bronze) by means of mechanical removal of casting clay and deposits):

1. removal of soluble fatty substances (washing with acetone),
2. preliminary elimination of hydrosoluble compounds and dust with distilled water,
3. elimination of deposits and corrosion products by Rochelle Salt treatment (saturated solution) for 3-4 hours, mildly stirring the liquid,
4. careful rinsing with distilled water to safety conductivity values (10-15 μSiemens) ("Rochelle" is a salt and once water conductivity returns to normal levels, it may be considered to have been completely removed),
5. temporary drying with a warm air current (40-50 °C),
6. localised finishing,
7. final rinsing with distilled water,
8. drying (as above),
9. rinsing with acetone (for complete water removal),
10. final drying,
11. recovery of the panel in a controlled environment (inert dry atmosphere).

Following the Rochelle bath treatment a few of the less accessible notches and hollows with thicker incrustations showed incrustation residues. These were diligently removed by the conservators with small point-like swabs saturated with Rochelle aqueous solution. On a few occasions on later treated panels, it was necessary to also employ the stronger alkaline Rochelle (Rochelle Salt to which a small amount of sodium hydroxide has been added), though in very limited areas. This reagent is more powerful and less selective than the former and must, therefore, be adopted only for localised use and followed by immediate rinsing (Colour Plate III.5, 6).

The long-term conservation problem after cleaning

After only approximately seven months, a very thin greenish veil of corrosion products began to manifest itself above the gilding (barely visible to the trained eye but clearly visible under the microscope) on the first cleaned panel kept in the laboratory and not yet in the controlled atmosphere box. This phenomenon, though slight, was not dangerous in itself but was worrying on a long term basis. Despite decontamination, the gold leaf/oxide/bronze system appeared out of equilibrium. Indeed, normal ambient humidity was sufficient to reactivate the galvanic and corrosive processes.

We could have thought of applying a protective coating to the gold. However, tests carried out resulted in a dulling effect and loss of expressive identity. Since there was no need to make a hasty decision (we had, after all, only just begun the compelling and predictably lengthy task of restoring the Paradise Doors) we opted to intervene upon the environment rather than upon the object itself. Once established that humidity was the main condition for degradation processes, it was decided to conserve the artefact in a humidity-free atmosphere. However, instead of choosing a vacuum environment, an inert gas ambience was preferred. With the help of technicians from the Institute Climatology Department, a tin-sealed plexiglas box was designed and filled with nitrogen at atmospheric pressure. The container was provided with a double base with grill into which silica-gel bags were lodged in order to keep internal humidity levels to a minimum. Any eventual tiny humidity infiltrations on the interior, in the case of imperfect sealing, would be absorbed by the silica-gel. Periodic maintenance was foreseen (nitrogen and silica substitution etc.). Plexiglas was preferred to glass for aesthetic reasons. It was not easy at that time to find glass without a greenish tint which gave the gold a cool tone. It must be pointed out that plexiglas is not the ideal material. Small quantities of volatile substances originating in the plastifiers added to the polymer may gradually contaminate the atmosphere within the container. Nevertheless, they could have been eliminated through periodic maintenance and, consequently, did not represent a real problem. Given the much greater choice of completely colourless glass today, this problem no longer subsists and plastic may be substituted with glass.

From the beginning of the 1980's when the first panels were conserved, and slowly and subsequently the other four, they were constantly kept in the containers in the Museo dell'Opera del Duomo in Florence. Over the years their condition has remained the same. The gold has maintained its re-acquired brilliance and unmistakable character. Considerable importance has been attributed to these factors. In those years, the completed Doors (two wings and remaining parts) were removed from Florence Baptistery and substituted by a gilded bronze copy, financed by a Japanese sponsor. The copy was produced from moulds made in 1948 after the previous restoration.

Conservation of the Panels and Frame Still Attached to the Doors

Six panels have been conserved to date. They were the ones which had become detached from the doors during the 1966 flood and which had been reattached with screws from behind. The conservation of the entire Doors could have been completed a considerable while ago had it not been for certain serious difficulties posed by panels and frame elements which were still mounted on the doors. It was a very difficult task to decide whether detachment of each piece from the doors should be attempted in order to carry out the cleaning of each piece separately with the tried and tested method (immersion in a bath and subsequent treatments), or whether to avoid detachment and create artificial tanks to contain the cleaning liquids in situ after laying the door horizontally. The former solution certainly seems more ideal though it presents the problem of detachment of the pieces from the doors, an undoubtedly invasive and dangerous operation.

Here are a few of the procedures discussed and evaluated:

1. Application of screws from behind the door through thread holes (at least three in each panel or cornice element). By tightening the screws, pressure may be exerted from behind on the perimeter of the piece until its detachment is obtained. This, however, poses many problems. One of them is the extremely invasive (perhaps we should say destructive) nature of the operation which requires making a large number of holes in the bronze door wings. Although less esteemed than the modelling, they are still of considerable historic worth. Then there is the problem of targeting specific perimetrical points of the panel with screws from behind, where the thickness is greater, so as to avoid putting pressure on thinner and weaker areas with the risk of causing cracks or lesions. This hypothesis has been discarded.
2. Application of screws from the front and extracting the pieces by traction. Again we are faced with the destructive action of making holes and this time in the immediately visible anterior area. This hypothesis also seemed improbable and was discarded.
3. Extraction of the panels and cornice elements, still by means of traction from the front, without the aid of holes and screws. In this case, a rigid counterform is placed in contact with the surface of the panel followed by application of a vacuum pressure so as to transform both elements into a single solid which may then be gradually extracted. Considering the rather precarious condition of the gilding, there is the fear of provoking damage if the counterform is not perfectly complementary.
4. Extraction of the panel by means of traction from the front without making holes but by fixing a metallic frame to the perimeter of the piece with adhesives, by far the best method (and, in fact, this intervention will be adopted) which entails removing the patina from the perimeter of each piece to ensure perfect adhesion (all the pieces have a perimetrical non-gilded bronze cornice approximately 1 cm thick). A metallic auxiliary frame will then be adhered, to which traction will be applied orthogonally to the surface.

The other hypothesis (undertaking the cleaning without detaching the pieces) poses a series of problems. It is by no means easy to create artificial tanks on the surface of the door in relation to the individual elements. The majority of pieces have fissures and small losses through which the agents in solution would pass and penetrate between the back of the pieces and the bronze frame. It could then be difficult to completely remove the reagents from this not easily accessible interstice with the risk of leaving residues within. All the other stages (both the various bath treatments as well as the final operation of conserving a panel in a controlled atmosphere while continuing work on another) would be hampered. For these reasons, support was given to the solution indicated in point number 4, the adherence of a counter-frame.

Preliminary tests simulating the feasibility of this hypothesis were carried out by our conservator Fabio Burrini in the laboratory. The chosen adhesive was a type of Araldit (epoxy resin) which was used to laterally adhere a metallic bronze element and a stainless-steel one. This adhesive offers an elevated resistance to traction, but due to its rigid properties, it is relatively easy to break the joint and liberate the pieces with a subsequent light lateral knock.

The procedure envisaged is the following. A metallic frame the size of the piece to be removed (panel or cornice) is made with four separate fillets linked together with bolts to form a single unit. This frame is then laterally adhered to the perimeter of the panel with the epoxy adhesive (the patina of the perimeter should be first removed to ensure good adhesion). Finally, gradually increased pressure is applied to the frame until the panel detaches itself from the door.

At this point, the four elements are disconnected by removing the bolts and, with a light tap to each, they are separated from the perimeter of the panel. Any possible adhesive residues on the border are removed with appropriate solvents.

The above described cleaning procedure may be applied on each of the individual pieces of the Doors. Once this operation is completed, the perimeter of the pieces will be re-patinated. This kind of intervention appears to satisfy the majority of requirements with the least risk of damaging the artefact as well as permitting the same cleaning procedure used for the other already conserved panels. This intervention is expected to begin in the coming months.

At the very end of the entire operation (all pieces completed including the two frames of the doors) the task of recomposing the Doors remains, thus reconciling the need for unison with conservation requirements. A suitably large and perfectly sealable container to insure the necessary inert atmosphere, will have to be designed.

Yet again, an invaluable and precious monument, conceived for an outdoor artistic-architectural destination, will be sheltered in a controlled climatic environment in a museum and substituted in situ by a copy. This seems to be the inevitable destiny of a large part of our outdoor cultural heritage.

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