



WG Metals and Glass & Ceramics

## Experts' Meeting on Enamel Conservation

1./2. July 2006

Château de Germolles, Cidex 407,  
F-71640 Germolles (Mellecey), France



Swiss Guard with flag, Jean Louis Giradet, Berlin before 1725. Green Vault Inventory number VI 81 a. Materials: Pearls, gold, enamel, silver partly gilt, diamonds, rubies, ivory. Height of figurine: 15.3 cm (photograph Green Vault collection)

# **The aims and outcomes of the meeting: Networking expertise in conservation**

## **Aims**

Multi-media objects present a challenge for conservators and conservation scientists, who may be specialized in only one of the component materials. Some conservators' organizations, like the Committee for Conservation of the International Council of Museum's (ICOM-CC) have different working groups (WG), for different materials-based specialties. But often multi-material objects in need of treatment cannot be separated. How to conserve an enamel without keeping effects on the metal support in mind?

That's why the WGs Glass & Ceramics and Metals started an initiative during the Triennial Meeting of the ICOM Committee for Conservation in The Hague Sept. 2005 to network expertise in both fields of conservation. A questionnaire to interested members drew many responses, mainly from all over Europe – and gave a clear picture: Although there was interest in many material combinations (e.g. leaded glass windows, historic metal staples in ceramics, etc..) the main interest clearly focused on enamel on metals. Much research has already been done, there are ongoing projects, but many felt that there are additional research needs.

It became clear then what to do: gather all this expertise in an 'experts meeting on enamel conservation' as a start. An invitation to Château de Germolles (F), the former home of the Dukes of Burgundy (14<sup>th</sup> century), patrons of the art of enamel, on the first weekend of July gave the ideal and historically inspiring setting for this workshop. Financial support from EU COST programme will allow experts from all around Europe and USA to take part independent of the travel budget of their institutions.

We hope that this meeting will form the nucleus for networking all this expertise in an interdisciplinary group which transcends the borders between the ICOM-CC Working Groups Metals and Glass & Ceramics. Improving existing literature databases, identifying research needs and inspiring cooperation, developing web-based communication for an experts network, future meetings (e.g. within the framework of existing conference series): there's so much that could be done in a joint effort.

## Outcomes

With all their different topics, all 19 lectures of the experts' meeting on enamel conservation had one thing in common: They illustrated impressively the wealth and importance of enamelled metal objects within our shared cultural heritage, the outstanding Limousin objects being just one example. Objects from Limoges are found in major collections all over the world and are studied continuously (e.g. in museums in Stockholm, London, and Krakow) and deservedly so. But be it the Baroque figurines of the Dresden Green Vault or the Burgundian silver goblets of Kunsthistorisches Museum Vienna, enamel poses special conservation problems. This led already in the 1990's to important national research projects with the aim of preventing further loss, which still guides current treatment and preventive conservation. But despite innovative concepts for prevention and treatment, practical solutions for display and conservation have still not been realized. Costly display cases are normally beyond the reach of local collections. Innovative treatment concepts like the ORMOCERs of the Fraunhofer Institute still need evaluation of their long term effects on enamel under real life exposure. Re-conservation has to face old treatments and their not always well known effects.

The metal part of the enamel/metal composite also needs more consideration. New metal corrosion products are still being identified. The effect of conventional corrosion inhibitors on enamel has to be explored. The bond at the metal/glass interface via surface oxides should be studied by modern advanced analytical methods. Here, the future involvement of experts from industry could prove fruitful. Compositional studies on both sides could lead to quantitative data on the differences in thermal expansion, which, after corrosion, is presumably the most important factor for the overall conservation state of these objects.

These desiderata must form the nucleus for future research, which should be accompanied by a permanent experts' network. The participants in Germolles therefore decided to form a group which is affiliated as a 'sub-WG' to both the WG Glass & Ceramics and the WG Metals of ICOM CC but stays open to all interested people. Gerhard Eggert promised to coordinate this effort until 2008, Agnès Gall-Ortlik will assist. Communication tools will be a special e-mail discussion list/newsgroup which can easily link and involve all experts. All relevant information should also be accessible on the existing webpages (ICOM-CC Metal and Glass&Ceramics WGs and the **METAL Consn-**info) for the conservation community. A first step will be to develop a knowledge base of the widely dispersed literature on enamel history, technology, and conservation. Gall-Ortlik's already existing bibliography of 2001 can form the starting point which should be updated and enlarged in a joint effort. In 2007, the Interim Meetings of the WG Glass & Ceramics in August in Slovenia and of the WG Metals in September in the Netherlands can bring together groups of enamel experts and serve as forums. European meeting options for 2008 are still open. The Triennial ICOM-CC Meeting in

New Delhi (Sept. 2008) with the business meetings of the WGs will allow a summary of achievements thus far and decisions about future actions.

The participants want to use the impact of the COST funded experts' meeting on enamel conservation in Germolles to create a fruitful and inspiring environment for the much needed further research aimed at our common goal: The preservation of our endangered rich heritage of enamel objects in Europe!

The Workshop Committee:

Gerhard Eggert, scientific co-ordinator of the conference

Christian Degriigny, ICOM CC WG Metals coordinator and conference organiser

Lisa Piloni, ICOM CC WG Glass & Ceramics coordinator

Hannelore Römich, COST Science Officer

## Themes covered

- 1) Technology & history of Enamels on metals
- 2) Analysis and diagnosis of enamels on metal
- 3) Corrosion studies
- 4) Preventive conservation
- 5) Conservation problems / case studies

## Programme

**Saturday, July, 1<sup>st</sup>, 2006**

**10.30am – 12.00 am**

Introductory statements:

*Gerhard Eggert*, conference co-ordinator  
Why this conference now?

*Christian Degrigny*, ICOM-CC WG Metal co-ordinator  
ICOM-CC and the Metal WG: importance of research  
dissemination towards metal conservators

*Lisa Piloni*, ICOM-CC WG Glass & Ceramics co-ordinator  
The Glass and Ceramics WG and enamels

*Hannelore Roemich*, Science Officer, COST Chemistry &  
materials Actions  
COST and conservation

Introduction of the participants

**12.00 – 1pm**

Light lunch

**1.00 – 1.45 pm**

Theme 1: technology & history of enamels on metals

*Maria Franzon*, SWEDEN  
Technical studies of painted Limoges enamels at the National  
Museum of Fine Arts, Stockholm

*Catia Viegas Wesolowska*, PORTUGAL  
Translucent enamels on silver: Examination of the metal  
substrate on a group of European XIV to XV century objects

### **1.45 – 3.10 pm**

Theme 2: Analysis and diagnosis of enamels on metal

*Mark T. Wypyski, USA*

Compositional analysis as an aid in the identification and authentication of enamels

*Marco Verità, ITALY*

The enamels of the Orvieto *Corporale*: manufacturing techniques and weathering phenomena

*Veerle Van der Linden, BELGIUM*

Chemical analysis of 16<sup>th</sup>-17<sup>th</sup> century painted enamels from Limoges: some preliminary results

*Lorna Calcutt, UK*

Cloisonné in context: Conservation issues related to Oriental cloisonné housed within two National Trust Collections

### **3.10 – 4.15 pm**

Theme 3: Corrosion studies

*Martina Griesser, AUSTRIA*

Study and conservation of strongly corroded translucent enamel on silver goblets, Burgundy, 15<sup>th</sup> century

*Patrick Storme, BELGIUM*

Research for stabilizing copper corrosion on enamelled works of art

*Gerhard Eggert, GERMANY*

Socoformacite: When enamel and metal corrode together

### **4.15 – 4.45 pm**

Coffee Break

### **4.45 – 6.10 pm**

Theme 4: Preventive conservation

*David Thickett, UK*

Preventive conservation of enamels

*Eckhard Rikowski, GERMANY*

Corrosion mechanisms and preventive conservation of Baroque enamelled jewellery

*Peter Mottner, GERMANY*

Green Vault Dresden: Glass sensors, Ormocers

*Rainer W. Richter*, GERMANY

Environmental control of consolidated crizzling enamels in the permanent exhibition of the Green Vault, Dresden

**6.10 – 7.00 pm**

Theme 5: Conservation problems / case studies

*Agnès Gall-Ortlik*, SPAIN

Research on the history of enamels on metal Conservation

*Andrej Šumbera*, CZECH REPUBLIC

Documentation and Restoration of Czech Enamel Treasures

**7.00 – 8.00 pm:** *Tour of Château de Germolles*

**8.00 – 9.00 pm:** *Wine tasting*

**9.00 – 11.00 pm:** *Conference dinner at Château de Germolles*

**11.00pm:** return to the hotels in Chalon-sur-Saône

**Sunday, July 2<sup>nd</sup>, 2006**

**9.00 - 10.00 am**

Theme 5: Conservation problems / case studies

*Pawel Karaszkiwicz*, POLAND

Two enamelled objects from the Krakow museum – case studies

*Stéphane Crevat de la Bollière*, FRANCE

Deposits and waxes applied on artefacts made of enamels on metals. Observations and questions of a conservator

**10.00 – 12.00 am**

Networking expertise in conservation – Discussion of further work

Organisation, bibliography, web-based communication, research cooperation, meetings...

## List of abstracts

Lorna Calcutt, UK

Cloisonné in Context: Conservation issues related to Oriental cloisonné housed within two National Trust Collections.

Anecdotal evidence suggests that late 19<sup>th</sup>-early 20<sup>th</sup> century Oriental cloisonné is perceived as relatively stable and robust. Though variable quantities of literature exist which describes art history, composition, manufacture and conservation issues there appears to be a lack of communication between all the interested parties. The project reports on varied investigations of objects of this date range housed within two National Trust properties. Research included discussion with art historians, contemporary makers, scientists and conservators. Each constituency added valuable insights and this highlighted the benefits of open discussion between all disciplines. Results suggest that the material may contain a certain inherent instability that may merit focused handling, storage and display criteria.

Stéphane Crevat de la Bolliere, FRANCE

Deposits and waxes applied on artefacts made of enamels on metals. Observations and questions of a conservator

During cleaning interventions on artefacts made of enamels on metals, the conservator might find deposits on the metal and/or the enamel. For the champlévé Limoges' enamels the knowledge of the composition and origin of brown deposits on the gilding and pink compounds within the pores of the enamel would contribute to the better understanding of the technology used to produce these artefacts and help the conservator in the choice of the level of cleaning.

The localization and identification of original coloured waxy fillings in the cloisonné Chinese enamels is essential before the cleaning step. Would the filling with charged and pigmented wax be an alternative to the conservation techniques currently employed that are based on the use of poorly reversible resins?

Gerhard Eggert, GERMANY

Socoformacite: When enamel and metal corrode together

A new corrosion product, a sodium copper formate acetate (abbreviated: socoformacite), could now be identified by XRD on three different enamel objects and on glass beads in contact with a metal wire on a Chinese theater hat (ca 1900) which has been stored for a long time in a wooden cupboard.



Hitherto, there was only one report of this corrosion product in the literature but only for pure copper alloy objects, most of them ancient Egyptian bronzes. They often develop a sodium copper carbonate (chalconatronite,  $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) as a corrosion product when logged in soda rich soil. Another source for sodium could be former conservation treatments (e.g. treatment of 'bronze disease' by storage in sodium sesquicarbonate solution or electrolysis in caustic soda for dechlorination). But our objects were neither soil logged nor conserved before. Sodium here clearly must originate from soda-lime glasses: In the presence of humidity and  $\text{CO}_2$  from the air, sodium can be leached out and deposited as sodium carbonate on the surface. The chemical environment is then similar to those for Egyptian bronzes. The reaction of copper and sodium species (either intermediate chalconatronite or the individual carbonates soda and malachite or dissolved sodium and copper ions) with trace emissions of formic and acetic acid from wood leads then over time to the formation of socoformacite, the first observed mixed corrosion product of copper and glass.

*Maria Franzon, SWEDEN*

Technical studies of painted Limoges enamels at the National Museum of Fine Arts, Stockholm

Technical studies of the painted Limoges enamels in the collection of the National Museum of Fine Arts in Stockholm were undertaken 2002-2004. The collection consists mainly of painted Renaissance enamels from the second half of the 16<sup>th</sup> Century and the first half of the 17<sup>th</sup> Century. The aim with the project was to address issues on authenticity and attributions. Micro-XRF analyses were therefore performed in situ by Dr Stefan Röhrs, Technical University of Berlin, in 2003. The results from the investigation were included in an exhibition (Falskt & Äkta) at the National museum in 2004, as well as presented at the 3<sup>rd</sup> International Symposium on Limoges enamels (Limoges September 2004).

*Agnès Gall-Ortlik, SPAIN*

Research on the history of enamels on metal conservation

Research on written and published historical texts on the conservation of enamels on metal is continued since the year 2000, with the goal of establishing a concise bibliography of available sources. The texts gathered allow to chronologically index ancient and actual treatments performed on enamels on metal.

The analysis of written material and (when possible) the study of the actual condition of the objects that have been treated in the past is an ideal occasion to realize their assessment, to compare them with actual approaches, and to point out some issues that would need urgent research.

Martina Griesser, AUSTRIA

Study and conservation of strongly corroded translucent enamel on silver goblets, Burgundy, 15<sup>th</sup> century

Within the collections of the Kunsthistorisches Museum, Vienna, a set of four silver goblets from Burgundy, 15<sup>th</sup> century, in large parts covered by red, green, and blue translucent enamel (émail en ronde bosse) is held. As part of a research project – performed from 1992 onwards – the severe degradation of their enamel decoration was studied in co-operation with the Academy of Fine Arts Vienna, the University of Applied Arts, Vienna, and the Vienna University of Technology. As the enamels were produced using a rather high proportion of flux agents (potash and soda) and only a comparatively small amount of silicon dioxide, they can be expected to be chemically fairly unstable. In addition, they developed micro cracks by mechanical tensions, presumably already directly after the burning process. Due to the influence of atmospheric moisture – also able to enter inside the cracks – enamel corrosion (dissolution of the alkaline components and decomposition of the basic silicate body) developed at the surface, in the cracks, and at the enamel/silver interface of silver applications. This corrosion caused discoloration (darkening) of the enamel, a loss of transparency, a matt surface appearance, white blooming, and together with further mechanical tension eventually the loss of big parts of the enamel due to a decreased adhesion to the silver support. The conservation of the objects, finished only recently, included their cleaning, the removal of former consolidants, and the consolidation of the enamel decoration using acrylic resins.

Pawel Karaszkiwicz, POLAND

Two enamelled objects from the Krakow museum – case studies

Research on two enamelled pieces from the collection of Czartoryski Museum in Krakow is described. In one case (the plate of Queen Anna Jagiellonka) the condition after previous conservation is evaluated, in the second one the evaluation of enamel corrosion on a Limoges enamelled small altar will be presented. The method of preventive conservation approach is suggested.

Peter Mottner, GERMANY

The Green Vault Dresden: Environmental Monitoring and ORMOCER Application on Enamel Artworks

Within a joint research project on damage phenomena observed at the precious gold enamel artworks in the Green Vault Dresden, the Fraunhofer Institute ISC performed sensor studies to evaluate the micro-climate within rooms and show-cases of the Green Vault collection, and developed and

taylored Ormocer® resins for successful and reversible consolidation and gluing applications of loose and flaked-off enamel fragments.

Especially the climate within sealed show-cases was found to be aggressive depending on high concentrations on formic and acetic acid together with humidity, causing and supporting the degradation and the exfoliation of the enamel surface layer.

For fixation of enamel fragments, the application of a special mixture of Ormocer®s together with Paraloid B72 was chosen as best practice after a screening campaign on various promising conservation products by accelerated weathering.

The environmental sensor method together with representative results, reflecting the potential of the commercially available product, and details of the Ormocer® application will be presented.

#### Rainer W. Richter, GERMANY

Environmental control of consolidated crizzling enamels in the permanent exhibition of the Green Vault, Dresden

Severely crizzled German gold enamels of the 17<sup>th</sup> and 18<sup>th</sup> c. in the Green Vault collection were consolidated by using an organic-inorganic hybrid polymer, Ormocer® OR-G50 + OR-B30. All consolidants for enamels, which meet the conservation requirements, do not act as an effective barrier for moisture or gaseous pollutants. Therefore the following measures for the design of the cases in the permanent exhibition of the Green Vault were recently taken for efficiently reducing the future rate of enamel corrosion:

- use of tested case construction materials
- relatively air-tight sealing of the case
- adjustable circulating air-flow system
- use of activated charcoal as a scavenger for gaseous pollutants
- use of silica-gel as a RH buffer
- long-term conditioning of the silica-gel by means of a commercial microclimate control unit with a low air-flow (for selected cases only)
- electronic control system

The results of the environmental performance of the chosen case design are discussed.

#### Eckhard Rikowski, GERMANY

Corrosion mechanisms and preventive conservation of Baroque enamelled jewellery

Due to corrosion processes baroque jewellery of the Green Vault in Dresden had been in danger to lose their colourful enamel layers. The adhesion of

these layers on the noble metal alloys got lost and brittle pieces of enamel could be found inside the showcases.

To find the reasons for these corrosion processes the chemical compositions of enamels have been analysed by EPMA on the one hand. On the other hand climate conditions and the level of air pollutants in the exhibition rooms and the show cases as well have been determined. In addition the emission characteristics of materials inside the exhibition rooms and the showcases have been analysed in emission chambers to localise the sources of emission. According to the analytical data found by EPMA model enamels have been prepared for further tests. These model enamels have been exposed to pollutants in climate chambers to determine the corrosion processes of different enamel compositions.

Due to the results the climate conditions in the exhibition have been improved and further damages of enamel layers can be prevented.

#### Patrick Storme, BELGIUM

Research for stabilizing copper corrosion on enameled works of art

The copper base of an enameled object can start to corrode when there is access for moisture and pollutants from the surrounding environment. The corrosion product can interact chemically with the enamel, and will always form a product that expands and puts physical stresses on the enamel layer. Removal of the corrosion product is very often impossible, so stabilizing can be a choice. The commonly known products for copper corrosion stabilization have limited properties of penetration and/or protection capacities. The research focuses on the use of Raman spectroscopy to look at the actual changes of the corrosion product beneath the enamel layer.

#### Andrej Šumbera, CZECH REPUBLIC

Documentation and Restoration of Czech Enamel Treasures

The presentation will focus on:

1. Restoration and documentation of the reliquary of Saint Maurus:
  - corrosion of enamels due to forty years of underground storage
  - options of modern ways of documenting this treasure.
2. Research of Czech coronation jewellery, restoration of the Golden Cross of Charles IV.
3. Illustration of documentation of enamels parts from the 10<sup>th</sup> to 18<sup>th</sup> centuries.
4. Presentation of interactive programs on CD-ROMs illustrating goldsmith works and their restoration. Possibilities of use in education process of restorers and goldsmiths.

David Thickett, UK

Protection of enamels on display

The Werhner Collection at Rangers House includes a fine collection of Renaissance enamels. The collection was redisplayed in custom built showcases in 2002. The environmental performance of these showcases has been assessed in terms of RH, temperature and their profiles across the showcases. Temperature profiles were measured across the surfaces of the enamel plaques with thermography. Pollutant gases were analysed. Analysis of the enamel surfaces showed the presence of sodium sulfate salts, and various copper corrosion products, but these were shown to be from the previous display and storage conditions. X-ray fluorescence analysis of the enamel glasses showed elemental separation of some elements, especially calcium and barium in those showing deterioration. The state of deterioration of the enamel surfaces was determined with non-interventive Fourier Transform infra-red spectroscopy with the intention of re-analysing at a future date to determine any ongoing deterioration.

Veerle Van der Linden, BELGIUM

Chemical analysis of 16<sup>th</sup>-17<sup>th</sup> century painted enamels from Limoges: some preliminary results

In order to elucidate the technological history of painted enamel (*émail peint*) the decorative layer of thirteen plaques was qualitatively analyzed by means of microscopic X-ray fluorescence spectroscopy ( $\mu$ -XRF). These non destructive analyses were supplemented with quantitative information obtained by analysing several small glass fragments of other painted enamel objects using Electron Probe Micro Analysis (EPMA). Most analysed objects originate from Limoges and are dated between the 16<sup>th</sup> and 17<sup>th</sup> century. The results of the analysed enamels were compared with a glass composition database containing 16<sup>th</sup>-17<sup>th</sup> century luxury and domestic tableware. Once this technological history is understood it is the intention to

- identify exceptional cases of painted enamel such as wrongly dated objects and later restorations and
- analyse other types of enamels upon metal to refine our expertise.

Marco Verità, ITALY

The enamels of the Orvieto *Corporale*: manufacturing techniques and weathering phenomena

The reliquary known as the Orvieto *corporale*, one of the most important masterpieces of Italian goldsmith's *art*, was made by the Sienese goldsmith Ugolino da Vieri in 1337 to preserve the corporal of the miracle of Bolsena of

1264 (drops of blood fell from the host during the mess). The reliquary is 1.39 m high and 0.63 m wide, and is made of silver. The engraved surfaces representing the various scenes, are covered with transparent coloured enamels applied with a technique probably invented in Siena in the 13<sup>th</sup> century. Effects of *chiaroscuro* and relief are given by the varying thickness of the glassy transparent layer.

The reliquary is in a bad state of preservation. More than 50% of the enamel is lost, mainly in the two front doors. Macroscopic investigations have shown a detachment of small glass particles, the presence of an extended network of micro-fractures, the existence of deposits on the weathered enamel surfaces.

X-ray microanalysis allowed the chemical composition of yellow, purple, green and blue enamels to be determined quantitatively on flaked particles. The mixed alkali composition allowed to identify the glass technology and the colouring techniques. Similarly, the composition of the deposits and of the glass weathered layers were determined.

The investigations allowed to identify the most important causes of deterioration, to suggest a cleaning procedure and to suggest an environment of preservation.

#### Catia Viegas Wesolowska, PORTUGAL

Translucent enamels on silver: Examination of the metal substrate on a group of European XIV to XV century objects

The purpose of this research is to identify the relation between enamel deterioration/loss and silver substrate. Causes may be related to expansion/contraction in metal, corrosion, poor surface preparation (low carving, etc). Results may help consider more suitable conservation treatments particularly preventive conservation, and prevent future deterioration of other contemporary objects. Other technological and historical questions will arise such as were goldsmiths aware of the properties of metal alloys and did they consider this in their enamelling work. This research will hopefully contribute to building a better picture of the work of the enameller/goldsmith in this period.

#### Mark T. Wypyski, U.S.A.

Compositional analysis as an aid in the identification and authentication of enamels

Compositional analysis can provide a wealth of detailed information for the provenance, comparison, dating and authentication of enamelled objects. A long term continuing program of analysis at The Metropolitan Museum of Art

has allowed us to gain information on Byzantine, Medieval, Renaissance as well as more recent enamel compositions. Using X-ray micro-analytical techniques, a wealth of reliable data has been obtained on hundreds of objects from the Museum's collection and elsewhere, working with minimally invasive samples, generally less than one cubic millimeter in size. Compositional analysis can also shed light on the history of enamelling technology and on the causes of enamel deterioration.

## **Conference CD**

COST will publish the Powerpoint presentations on a collective non-commercial CD.

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