Influence of the 2003 heatwave on the corrosion of Silver in museums

Michel DUBUS *, Christophe MOULHERAT**, Laurianne ROBINET***, Helen SPENCER***

* Preventive Conservation Department / Centre de Recherche et de Restauration de Musées de France, ** Centre Européen de Recherche des Textiles Anciens, *** Conservation and Analytical Research Department / National Museums of Scotland

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Introduction

The influence of the climate and of the atmospheric pollution during the 2003 heatwave on the corrosion rate of Silver is part of a program of surveys in several French museums : Musée du Louvre (département des objets d'art, département des sculptures), Musée national du Moyen-Age, Musée national des arts asiatiques, worried by the conservation of their silversmith collections.

Experimental

The corrosion of Silver has been studied from October 2002 to October 2004 in an exhibition room and two showcases to evaluate their efficiency towards the pollutants; the methodology is based on the resistivity measurement of Silver strips and on the characterization of the corrosion products of Silver, Copper and Lead coupons analysed by low incidence x-ray diffraction (XRD); the nature of the pollutants can be infered through the chemical composition of the corrosion products. This methodology has been developped in 2001 [1-3] and applied in 2002 in the conservation studios of the C2RMF [4-5]. Temperature and relative humidity have been recorded with data loggers.

The methodology for accelerated corrosion testing of Silver, Copper and Lead exposed to the display materials [6] has been applied at the Conservation and Analytical Research Department of the National Museums of Scotland and completed on one hand by the characterisation of the corrosion products of Copper, Silver and Lead by XRD at the C2RMF, on the other hand by the expertise of the textiles at the Centre Européen de Recherche des Textiles Anciens after the methodologies described in [7-8].

The outdoor concentrations of O_3, NO_2, SO_2 have been recorded by Airparif, the organisation responsible for monitoring air quality in the Paris region [9].

The red showcase of Martin-Guillaume Biennais (1764-1843) has been chosen because it displays part of a silver gilt tea service (OA 9537) created by Biennais for Napoleon in 1810, the other part being exposed at the NMS in Edinburgh. This 150 years old showcase is made of a veneer of mahogany on a structure of oak, the inside being decorated with a red silk textile stretched on medium.

The green showcase of Jean-Jacques Feuchère (1807-1852) has been chosen because the feature of the gilt "seau à rafraîchir" is complicated and particularly difficult to clean. This showcase is over 100 years old; it is made of oak decorated with green "felt" stretched on medium. Measurements were also made in the room 79 where this showcase is located.

Results

Kinetics

The mean corrosion rate calculated over a 693 days exposure is 32 nm/month in the red show case, 50 nm/month in the green showcase, 76 nm/month in the room 79, corresponding to the “S4” Purafil’s classification for Silver, meaning a severe contamination of the atmosphere [10-11].

The plot of the corrosion thickness evaluated with resistivity measurements shows two phases, before and after summer 2003: from October 2002 to September 2003 the corrosion rate is identic in the room 79 and in the green showcase, twice the corrosion rate of the red showcase. From September 2003 to September 2004, there is an acceleration of the corrosion rate in the room 79, two times greater than in the showcases. An acceleration of the corrosion rate can also be observed in the green showcase one month after, this interval of time perhaps corresponding to the “inertia” of the showcase.

A succession of parabolic looking shapes separated by breakdowns can also be observed in the curves. To verify this possibility, the curves have been ploted in function of the square root of time. In the room 79 the different sections of the curve are linear, the kinetics is parabolic indeed; therefore the corrosion rate is controled by diffusion mechanisms. The corrosion rate is almost the same before and after the first breakdown, but it increases after the second breakdown, which corresponds to the period after the heatwave. In the green showcase a period of induction can be observed, during which the kinetics are not controled by parabolic laws, probably because the corrosion layer is too thin (less than 10 nm) due to the existence of an electric field [12]. A second phase during which the parabolic law can be applied corresponds to the 2002-2003 winter. After this phase the diffusion law cannot be applied. In the red showcase the same phenomena can be observed, but with a lower amplitude.

Corrosion products of Ag, Cu, Pb

In the three environments, Silver corrodes to form Silver Sulfide (Acanthite Ag_2S), Copper corrodes to Copper Oxide (Cuprite Cu_2O), lead to Lead Carbonate Hydrate (Hydrocerussite $2Pb3(CO_3).Pb(OH)_2$ and Plumbonacrite $Pb10(CO_3)6O(OH)_6$); in the green showcase Lead corrodes into Lead Acetate Hydrate $[(CH_3COO)2Pb.3H_2O]$. Calcite ($CaCO_3$) has also been detected in the room 79, probably because of the dust introduced from outdoors by the shoes of the visitors.

Discussion

Why different corrosion rates in the different environments? Why different corrosion rates in a same place at different periods of time? What is the origin of the corrosion: the climate, the display materials, the urban pollution?

Climate

Indoors the climate is stable all along the spring and the summer, from the 11th of March to the 23th of August 2003; there is no change before and during the heatwave.

In the room 79 and in the Biennais displaycase the mean temperature is 23$\pm$1°C, with a minimum of 19°C and a maximum of 26°C; the mean relative humidity is 45$\pm$2%, with a minimum of 37%, a maximum of 52%.

In the Feuchère displaycase the mean temperature is 24$\pm$1°C, with a minimum of 20°C and a maximum of 27°C; the mean relative humidity is 50$\pm$7%, with a minimum of 31%, a maximum of 62%. A close up to the climate in the room 79 in August shows that the temperature is much lower and stable than outside.

Display material, red silk

Visually the 3-1 test is negative on the red silk.

The warn of the red « silk » is made of mercerized cotton. In cross section , the fibres have nearly circular sections and contain smaller lumina than raw cotton. In longitudinal view , mercerized cotton appears markedly different from raw cotton in the degree of swelling and convolution of individual hairs.

The weft of the red « silk » is made of degummed silk; in cross section , they look like equilateral triangles with rounded apices. Under the action of severe rubbing or flexing, the filaments tend to show internal striations due to splitting into thin fibrils. In longitudinal view the degummed silk filaments are thin, uniform, and without internal structure.

Display material, green felt

The green « felt » of the green showcase is made of 90% of wool and 10% of polyester. In cross section the wool fibers are oval, the thinner fibres have a contour closed to a circle and are free from medullar canal. In longitudinal view a scale pattern can be seen at the surface of the wool fibres. The wool is responsible for the emission of sulfur compounds harmfull to Silver. In cross section , polyester fibres are circular with dulling particles. In longitudinal view , they are uniform in diameter along their length .

Materials 3-1 testing

The test is visualy positive on the green felt for Silver (2) and Copper (½), negative for the Lead. The corrosion products of Silver is Acanthite (Ag2S), Cuprite (Cu2O) and Tenorite (CuO) on Copper. Hydrocerussite $2Pb3(CO_3).Pb(OH)_2$, Plumbonacrite $Pb10(CO_3)6O(OH)_6$ and Lead Acetate Hydrate $[(CH_3COO)2Pb.3H_2O]$ have been identified on Lead.

Urban pollution

In Ile de France the summer 2003 has been marked by an important ozone pollution in relation with the heatwave.

“This phenomenon occurs when a chemical reaction takes place between nitrogen dioxide and hydrocarbons (motor vehicle pollutants). This reaction requires particular climatic conditions: strong sunlight, high temperatures, little humidity, little wind, temperature inversions” [9]. These conditions met during the heatwave of 2003; the air quality "ATMO index" determined with levels of pollution measured during the day by urban and peri-urban stations for background pollution in the city, identifies the typical characteristics of the overall air quality for the whole of the Paris region, and shows the relationship between the temperature and the quality of the air". During 12 days the concentration of ozone has exceeded $200µg.m^{-3}$.

Summary

Mechanisms

The corrosion products are not protective on the long term.

Outdoors the climate can be responsible for the formation of ozone, a strong oxidiser.

Indoors the corrosion of Silver is accelerated by the dust and the pollutants coming from outside and by internal pollutants like sulphur compounds from the wool and organic acids from the wood.

Solutions

In permanent exhibitions the display cases are built to last. If it is impossible to change them, they can be improved. We propose at the end of each study to modify one showcase with tested and accepted display materials and to make a small test to find out whether the improvement is succesfull or not.

For the temporary exhibitions we ask for technical data, we propose display materials testing when possible and systematically recommend the use of absorbers.

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