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"Conservation of Metal Statuary & Architectural Decoration in Open-Air Exposure"

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DIALOGUE/89 — The Conservation of Bronze Sculpture in the Outdoor Environment:

A Dialogue Among Conservators, Curators, Environmental Scientists, and Corrosion Engineers

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The Environment and the Future of Outdoor Bronze Sculpture: Some Criteria of Evaluation

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Abstract

Recent studies on deterioration of bronzes in outdoor exposure have improved knowledge on formation, constitution and properties of corrosion patinas and on some environmental parameters influencing electrochemical corrosion.

In a polluted area it is possible to calculate a damage function, from deposition intensity values for some air dispersed chemical compounds and local time of wetness for year (tw), measured for the metal surface.

tw has been determined utilizing a new, original instrumentation, developed by the laboratory of Chemistry of the Istituto Centrale per il Restauro in Rome.

Research must continue in some particular fields, as, for example, for a selection of new, long lasting surface coatings. In particular cases of surface deterioration and structural decay, it is quite compulsory to remove bronze statues from the outdoors, in order to conserve them in a "safe" environment.

This paper also presented at the 11th International Corrosion Congress—Innovation and Technology Transfer for Corrosion Control, April 1990, Florence, Italy, sponsored by NACE and the Italian Association of Metallurgy.

Introduction

Conservation of bronzes in outdoor exposure has become - in Italy - an urgent and current problem, because of the increasing damage, partially caused by air pollution, because of the need of a better understanding of the decay processes and finally for an appropriate appreciation of the artistic quality of artificial and natural patinas.

In the last years some important sculptures have been removed from outdoors:

1. In 1966 statues of the Griffon and Lion from the facade of Priori Palace in Perugia.
2. Beginning in 1974, the four Horses of St. Marco's Basilica in Venice.
3. In 1979-83-85 four bronze panels from the Door of Paradise, of Lorenzo Ghiberti, Baptistry of Florence.
4. In 1986 the statue of Judith and Holofernes by Donatello, from Piazza della Signoria, in Florence.
5. In 1981 the equestrian monument of Marcus Aurelius was transported from Piazza del Campidoglio in Rome, to the Istituto Centrale per il Restauro in S. Michele; after restoration, studies and discussions are now promoted, in order to indicate the future destination of the bronze masterpiece.

From this list, three monuments are gilded; moreover the Griffon and Lion preserve, in sheltered areas, some important remains of gold leaf, applicated with an oil mordant[1].

Recent studies point out that during electrochemical and chemical corrosion nucleation and cementation of the patina take place; the patina is mainly constituted - in a polluted atmosphere - by cuprite and brochantite, but also by antlerite[2,3] and, in some cases, by soluble calcantite[4], due to an increasing acidity of water in contact with the surface.

Time of wetness. Experimental procedure and results

The surface decay and discoloring of many important monuments have brought about in recent years an increasing amount of public interest and a more systematic scientific study in the field, for quantifying corrosion processes, and for obtaining a damage function correlated to time of wetness of the surface, as well as to some specific air pollution agents, promoters of corrosion[5,6].

Research carried out by the Laboratory of Chemistry of ICR in 1987-88 has been successful in designing and testing a new apparatus for measurement of time of wetness of a bronze surface, due to microcondensation into the patina layers[6].

Philosophy of the method has been discussed and developed in collaboration with CNR Center of Rome.

Instrumentation is made up by:

- Two silver electrodes (S1, S2) pressed against the surface by means of dynamometric springs, for measuring conductivity at different RH levels (figure 1). Electrodes are contained into a climatic microchamber (c) (figs. 1,2), which is placed onto the surface, obtaining a sealed space, into which RH can be increseased at different rates or maintained at a fixed level.
- Relative humidity is modified and/or maintained by an humidifying system with a pressure regulator (d).
- Values of conductivity and RH are read by a multimeter (b), on line with a computer (a).
- The computer is the operating center of the instrumentation: it programs and runs automatically the experiment, stores data, performs statistical analysis and produces graphic representations of the function c (conductivity) = f (RH), c = f (time).
- A third electrode (S3), in contact with a bare bronze area (fig. 3), measures - if coupled with S1 or S2 - also the volume conductivity of the patina.

At the end of the research, it has been possible to identify, for a case study, the Marcus Aurelius monument, some threshold values of RH, for the beginning of water vapour condensation into the capillary structure of the patina, causing a steep increase of conductivity, due to the organization of a continuous low resistance layer.

After about 150 experiments, an average threshold value of RH for the beginning of condensation and consequently of corrosion has been identified (~80% RH). As an example, in figure 3 it is represented a typical trend c (surface conductivity) = f (RH), for increasing values of RH; in figure 4 volume conductivity and RH are plotted, for a thin, permeable patina.

From the experimental data and from statistical summaries of weather data for the historic center of Rome, total time of wetness of the monument has been calculated, which is substantially the sum of wetness events due to rain falls and to condensation: tw is $\sim$ 0.22 year.

Damage function

For estimating electrochemical corrosion, a modified damage function described by Benarie and Lipfert, discussed in a former paper[6], has been applied:

$$M = tw \cdot 0.38 \cdot f\,(\phi SO_2 + 1.1\,\phi Cl^-) \qquad (1)$$

M is corrosion rate (g/m^2 for year); tw = 0.22; $\phi\ SO_2$ and $\phi\ Cl^-$ are the integrated fluxes or deposition intensities in mg/m^2 day, f is a factor (0.5) representing a dilution effect, of the gaseous pollutants ,due to the height of Campidoglio Hill, far from the exhaust of emissions of vehicles and other air pollution sources.

By using an average concentration value for SO_2 obtained by data of 1987-88[7] and an average deposition intensity value for chloride ion by IRMA project[8], equation (1) becomes

$$M = 0.22 \cdot 0.38 \cdot 0.5\,(33.4 + 1.1 \cdot 11.8) = 1.9\ g/m^2 \cdot year \qquad (2)$$

which means a corrosion $\sim$ 0.2 μm/year. Therefore electrochemical corrosion of the alloy is quite limited; in any case it is worthwhile to observe that the calculated value does not take in account integrated deposition fluxes for ammonium salts, acidic suspended particles, ammonia and nitric acid, all chemical agents activating electrochemical and chemical corrosion of the surface. In the last years (in particular at the beginning of '80) this value was probably equal, more or less, to 0.5 μm/year, for the higher level of SO_2[9].

Air pollution and corrosion

Damage function is valuable for calculating - with sufficient approximation - the rate of electrochemical corrosion. Damage function must be considered a simple way for judging deterioration process of a bronze alloy in an outdoor exposure, in addition to XRD analysis of patinas and metallographic examination. Deposition intensity of air pollutants onto corroded surface is much more useful for studying electrochemical corrosion than absolute concentration in the air.

Integrated flux ϕ or deposition intensity ($g/cm^2\ s$) is correlated to vd (velocity deposition, cm/s) and c ($\mu g/m^3$) in the following equation:

$$vd\ \ c/100 = \phi \qquad (3)$$

vd is dependent on some weather and microclimatic parameters and on mechanisms influencing transport and deposition of air pollutants (as, for particles, gravitational settling, thermophoresis, simple diffusiophoresis, Stefan flow, inertial capture[10]).

Rain water influences the decay of the surface, not only by increasing tw, but also by damaging it mechanically and partially by solubilizing some corrosion products.[11].

Statues after restoration are sometimes rapidly stained and covered by deposition of several air pollution agents, from different sources. For agent i, the concentration near the monument - tested in the sample k - can be represented as:

$$c_{ik} = \sum_j a_{ij} \cdot S_{jk} \qquad (4)$$

In this expression, aij is the fraction of component i, in the total emission of source j, and Sjk is the contribution of source j to the sample k.

So, for judging the importance of the different emission sources on surface loss it can be useful to calculate correlation coefficients between the different air pollutants and to carry out statistic analysis of the results, as for example cluster method or common factor analysis[12].

In this way it would be possible - for artistic buildings and monuments - especially in the old center of historic cities, to apportion air pollutants to the different sources, to identify distribution and intensities of the same sources, in order to judge in advance efficacy of some political strategies and interventions, for ammeliorating city environment.

Analysis of air pollution agents, accelerating electrochemical corrosion, and calculation of damage function are not sufficient, sometimes, to obtain an exhaustive description of the state of conservation and of the decay processes of a bronze in outdoor exposure.

It is evident that for some specific cases it is urgent to determine also quantitatively the chemical corrosion of the patinated surface, exposed to natural decay and to the action of some acidic air pollutants.

Controls can be activated by color macrophotographic documentation of surface specimens or by analysis of cations and anions contained in run-off water (in analogy to the measurements carried out for stone artifacts).

Researçh in this field has been carried out by Nassau[11], on samples of patinated copper, concluding that the most common patina products are substantially stable at a $pH > 2.5$.

Some problems of conservation

An urgent and difficult current problem of conservation is presented by gilded bronzes in outdoor exposure. In fact, as a consequence of electrochemical corrosion, gold leaf is not securely attached to the patina products and therefore it is easily detached and washed away by rain water. Furthermore, in these cases it is dangerous to treat the surface with corrosion inhibitors such as benzotriazole, for density changes of the reaction products.

Also some artificial patinas of modern bronzes, created for surface embellishment and artistic purposes, can be stained, discolored or dissolved, if not sufficiently sheltered from rain water and acidic air pollutants.

Another problem arises from the corrosion of iron armature bars in the clay core inside bronze castings. These iron bars - in contact with damp air or clay core - corrode with increasing specific volume, causing mechanical failures, cracks, and expulsion of dowels; in some particular cases, such as for the Angels of the facade of the Orvieto Duomo, protection of the damaged wings is impossible and protection of the bronzes inside a Museum becomes compulsory[13].

Another problem of structural decay is offered by the Medioeval door of S. Zeno in Verona. Bronze panels are crudely fastened to the wood structure and undergo mechanical stresses due to alternate expansion and contraction of the wood support[14] (for absorption and respectively evaporation of water). In this case, acoustic emission has been demonstrated as a valuable tool for studying, in real time, the stress processes of bronze elements, and the consequent structural damages.

Many other techniques can be adopted for analyzing defects and typical damages of bronze monuments[15]; a summary of non-destructive methods is presented in table 1.

Surface coatings

Another difficult problem is the selection of a long lasting coating, as a surface barrier and insulating layer against corrosion. This coating must guarantee 15-20 years protection, allowing maintenance.

Problems related to coatings have been extensively treated in a recent Symposium[16]; Selenia Industrial Group, in collaboration with Istituto Centrale per il Restauro, is carrying out a research in this field, testing eleven surface coatings, some of new formulation. Ageing of bronze samples, treated and untreated, is carried out by dry-wet and thermal cycles, by exposure to a Xenon lamp, and finally by using a spray chamber and a sodium chloride, acidic solution.

Controls and measurements for checking coatings are: ASTM Standards visual tests; cross-cut test; IR and UV spectrophotometry; thermal analysis; contact angle measurements; microbiologic controls; SEM + EPMA; solubility experiments.

At the end of 1989 results and conclusions will be available.

Conclusions

A satisfying, rational, long lasting conservation of monumental bronzes in outdoor exposure is not always possible, over all for artistic patinas and gilded surfaces in polluted atmosphere.

Some further research is required for obtaining:

- a better calculation of damage function
- a practical procedure for measurement of chemical corrosion
- a better knowledge of mechanisms of formation of some patina components as copper oxalate, calcantite etc.
- a better knowledge of composition and properties of artificial, artistic patinas
- a theoretical model of restoration, for cleaning, retouching and integrating bronze patinas
- study and adoption of new long lasting surface coatings.

Nowadays, if risk conditions are identified for bronzes with artistic, original patinas or gilded surfaces, and if structural, complex decay is in progress, conservation of artifacts inside a museum becomes compulsory.

If this resolution is a sign of our temporary defeat, it is also, from another perspective, a sign of our better multidisciplinary knowledge of decay models and of our professional attention devoted to problems of skillful conservation of artistic bronze heritage[17,18,19,20].

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Table I

X-rays	Gamma rays	Ultra sonics	Eddy c.	Interfe rometry	Strain gauges	Acoustic emission	Thermo vision	Hardness testing	XRF	ICC	Photo grammetry	Endo- scopy	// Documentation of:
											+		Form
											+		Outside surface
								+					Surface hardness
			+										Corrosion thickness
												+	Inside surface
+	+											+	Core armature
+	+											±	Soldered joints
+	+		+										Defects in s. joints
+	±		+										Superficial cracks
+	+												Deep cracks
+	+												Gas blowholes
+	±	±											Restraint defects
+	+	+											Thin areas
+	±	+											Thickness variations
+	±		+										Dowels
+	±												Lead particles, inclusions
									+	+			Alloys composition
							+						Thermal gradients
				+	+	+							Structural damages and deformations

Legenda: Eddy c.= Eddy currents ; XRF = X-ray fluorescence analysis;
ICC = conductivity of induced currents .
\+ = good information level ; ± = limited information level.

FIGURE 1

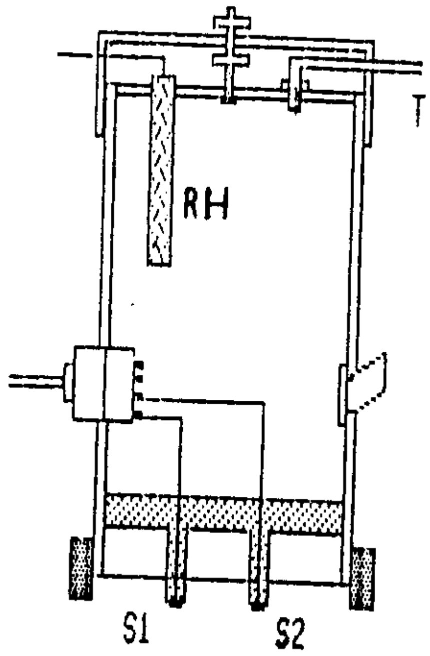

FIGURE 2

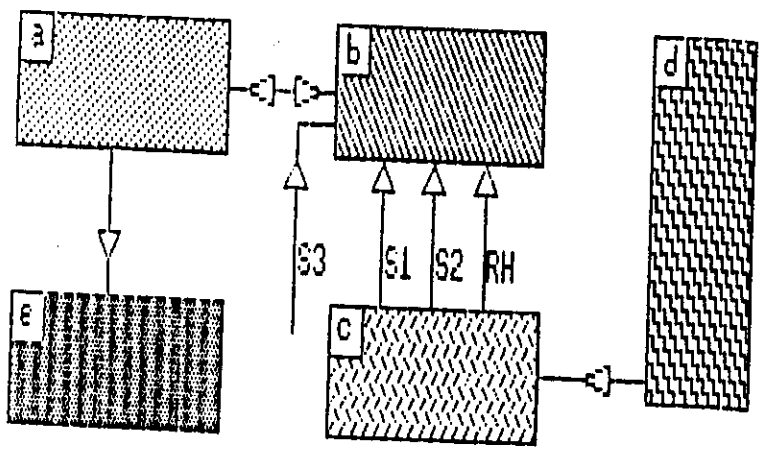

FIGURE 3

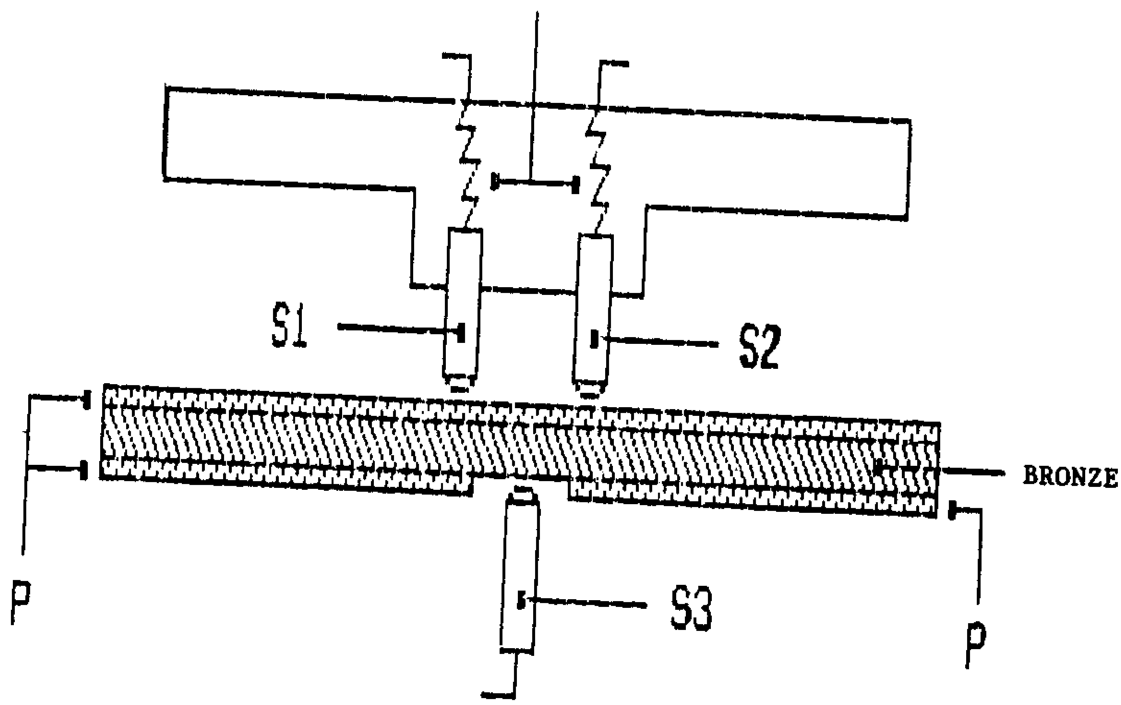

FIGURE 4

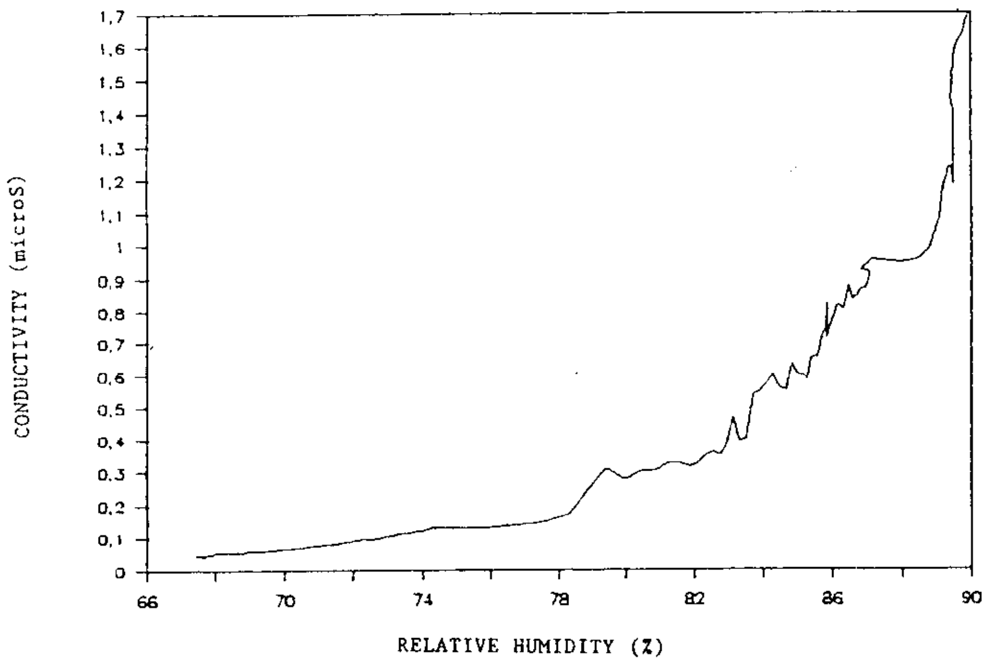

FIGURE 5