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BEHAVIOUR OF A GALVANIC CELL SIMULATING THE ATMOSPHERIC CORROSION CONDITIONS OF GOLD PLATED BRONZES*

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IN THIS paper some results of the studies carried out in this Institute concerning a corrosion system simulating the behaviour of gold plated bronzes exposed to the atmosphere are given.

The system consists of a "sandwich" formed of bronze covered by its artificially obtained corrosion products, on which a high porosity gold film is finally applied (Fig. 1). This system forms a galvanic cell which may be short-circuited so as to reproduce the corrosion phenomenon; the current thus measured by a zero resistance ammeter provides instantaneous and continuous information on the corrosion rate of the bronze.†[1,2]

As it is possible to measure currents from *ca.* 10^{-9}A upwards, corrosion rates equal to 1 mm/million years on a specimen whose exposed area is 10 cm^2 can be measured. The working conditions (with particular regard to: presence—or not—of condensed water on the gold coating, relative humidity, presence of pollutants and their amount, presence of corrosion inhibitors, temperature and differences of temperature between the system and the room, etc.) can either be varied as desired in the laboratory, or be the actual conditions in which gold plated bronze works of art are exposed to the atmosphere.

Therefore, the system thus set up is a rationalized model of the real systems and it is possible to achieve the following aims:

(i) to measure the corrosion rate in different conditions, specifying in particular the influence of the above mentioned factors;
(ii) to check the effectiveness of the proposed methods for the protection of gold plated bronze works of art, such as in particular: control of the r.h., use of inhibitors, heating, etc.;

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†The short-circuit current of the system of Fig. 1 may be assumed to equal the dissolution rate of the bronze, the "local processes" on the bronze itself being negligible also in consequence of the coupling with the gold (positive differential effect).

The electrochemical reactions corresponding to the operation of the galvanic cell of Fig. 1, may be represented schematically as follows:

$2Cu + H_2O = Cu_2O + 2H^+ + 2e^-$ at the anode (bronze),

$\frac{1}{2}O_2 + H_2O + 2e^- = 2OH^-$ at the cathode (gold).

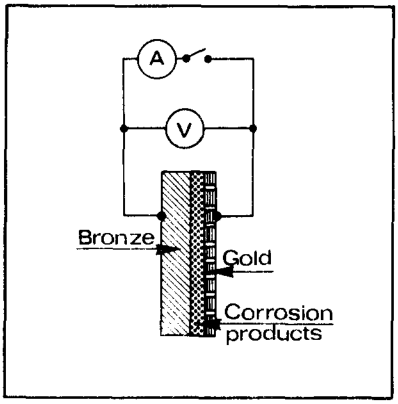

FIG. 1. Scheme of the corrosion system: bronze/artificial corrosion products/porous gold plate.

(iii) to define the electrochemical aspects of the behaviour of the real systems, so as to determine on the one hand the driving force available for the occurrence of the corrosion process, and on the other hand the type of kinetic control (anodic, cathodic, or ohmic) of the process itself, thus throwing light on phenomena which are also of general interest in the field of atmospheric corrosion.

EXPERIMENTAL METHOD

Details of the experimental techniques used for artificially forming the patina of corrosion products,* for preparing the gold plates† and for assembling the system, have already been described elsewhere.[1,3,4] Here it is only necessary to emphasize that the curves and the figures given below have a merely qualitative value and may differ from one specimen to another even by one order of magnitude, the working conditions remaining unchanged, because of the following reasons (in order of importance):

(i) above all, differences in the composition of the artificial patina of corrosion products as regards the presence of hygroscopic salts, ascribable to the preparation procedure (rinsing, etc.);

(ii) secondly, differences in contact area between the gold plate and the patina underneath;‡

(iii) lastly, differences in porosity of the gold plate.§

*This artificial patina (*ca.* 70 μm in thickness) consists of basic copper sulphates which have compositions similar to the naturally formed ones analysed by Vernon.

†The gold plates (*ca.* 20 μm in thickness) were deposited on an inert support by the vacuum evaporation technique.

‡The gold plates were fixed on the patinas of corrosion products with common glue spread around their edges.

§The porosity of the gold plates was determined by means of electrographic tests and of scanning microscope observations. A very large number of pores whose diameter was $< 1\,\mu m$ was found to be present, as well as small holes *ca.* 10 μm dia.

EXPERIMENTAL RESULTS AND DISCUSSION

The main results obtained can be summarized as follows.

(i) For the system placed in non-polluted air (in particular in the absence of sulphur dioxide) the corrosion current increases sharply with the relative humidity, above a critical threshold of *ca.* 60–70% of the latter (Fig. 2). In the presence of condensed water on the gold plate, the corrosion current is of one or several orders of magnitude higher. This behaviour applies to short exposure times, e.g. of 24 h.

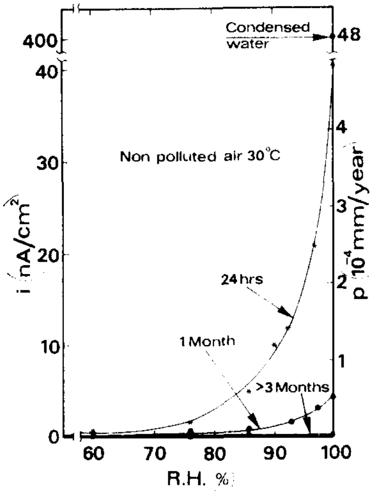

FIG. 2. Short-circuit current of the system of Fig. 1, as a function of the relative humidity (r.h.) and of the exposure time in non-polluted air at 30°C. On the right hand ordinate axis, current density (*i*) values are converted into penetration rates (*p*).

The voltage vs time curves after switching off the circuit show that the driving force available for the current flow in the short-circuited system (several tens of mV) is dissipated only to a very small extent in the form of those contributions which disappear instantaneously, such as, in particular, the ohmic drop. On the other hand the introduction of suitable reference electrodes in the short-circuited system shows that the overall corrosion process is cathodically controlled, as confirmed also by the steepness of the polarization curves of anodic dissolution of bronze covered with its artificially obtained corrosion products and of the polarization curves of cathodic reduction of oxygen on gold in suitable solutions.[3]

(ii) For the system initially placed dry in non-polluted air at a given r.h. value, the plot of the time dependence of the corrosion current at first shows an increase corresponding to water absorption, until a maximum is reached after a few hours. Then the corrosion current decreases slowly but continuously in time (Fig. 3). For instance, after one month of operation, values of one order of magnitude lower than those referring to an exposure time of 24 h are reached, and after three months the corrosion current becomes practically negligible even at 100% r.h. and in the presence of a liquid layer (Figs. 2 and 3).

As far as this effect which occurs after long times of operation (the "ageing" effect) is concerned, it is related to formation of corrosion products (e.g. cuprous oxide) in

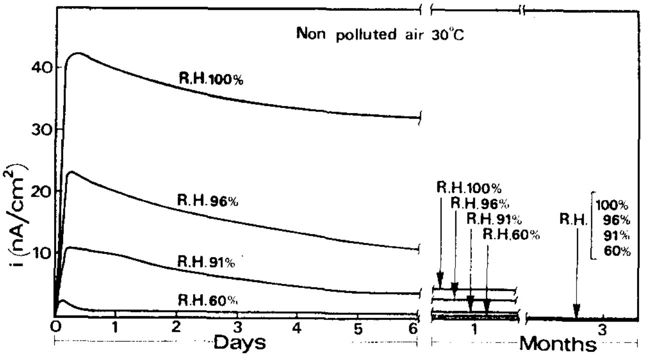

Fig. 3. Plots of the time dependence of the short-circuit current of the system of Fig. 1, initially placed dry in non-polluted air at different values of r.h. and at 30°C.

correspondence to the gold plate pores, which hinders the oxygen reduction process.

(iii) In non-polluted air the lowering effect on the corrosion rate produced by suitable corrosion inhibitors (2-mercaptobenzothiazole and benzotriazole were employed) is not very considerable (Fig. 4*), except in the presence of condensed water (exposure time 24 h). Specifically referring to this latter case, experiments have been performed with the system operating for longer times in distilled water, in order to check the permanence of the beneficial effect. After about one month of operation the beneficial effect of the considered inhibitors vanished.

(iv) In non-polluted air and in the absence of condensed water on the gold plate, the overheating of the system with respect to the room temperature as schematically shown in Fig. 5, causes the corrosion current to diminish: the higher the r.h. is, the higher the decrease in the corrosion current (Fig. 6). This effect is consistent with the hypothesis that a moderate overheating locally lowers the relative humidity in the air film in contact with the gold plate or inside its pores, as well as inside the patina of corrosion products; this lowering opposes and overcomes the acceleration of the rate of the electrochemical processes.

(v) Outdoor measurements in the urban–industrial atmosphere of Milan (Table 1) have shown that the lowering effect on the corrosion rate caused by the "ageing" of the system during its operation may vanish (i.e. the galvanic current begins flowing again when the environmental aggressiveness exceeds a certain limit). Moreover, any effectiveness of the corrosion inhibitors fails, whilst the overheating of the system with respect to the ambient temperature remains favourable in the absence of rain which continuously renews the liquid layer on the gold plate.

In particular, peaks in the corrosion current appear in correspondence to wet fog or damp smog conditions,† when the specimen is covered with a film of low pH moisture, but even in these conditions the effect of the overheating is beneficial.

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*By comparing Figs. 2 and 4, with reference to the curves marked "24 h" and "N.I." respectively, it may be observed that the differences in corrosion current of specimens with different preparation procedure are considerable. The specimens utilized in the tests of Fig. 4, which show very low values of corrosion current, have been carefully rinsed before being assembled, so as to remove most of the hygroscopic salts from the artificial patina of corrosion products.

†The specimens were sheltered from rain or snow.

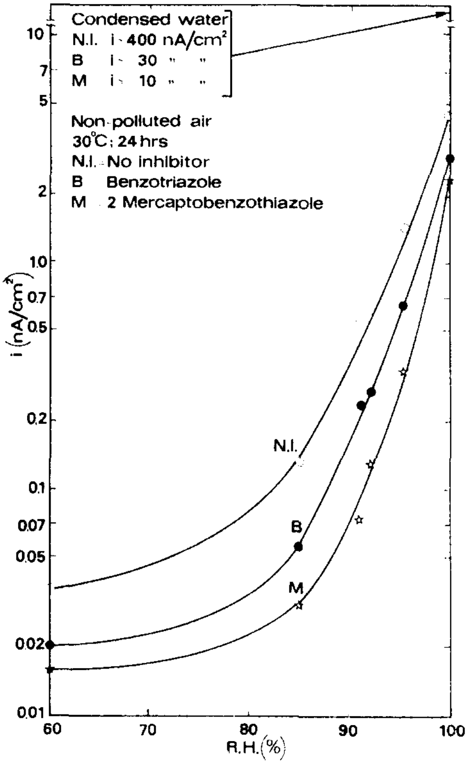

FIG. 4. Effect of the corrosion inhibitors 2-mercaptobenzothiazole and benzotriazole on the short-circuit current of the system of Fig. 1, as a function of the r.h. in non-polluted air at 30°C, for an exposure time of 24 h.

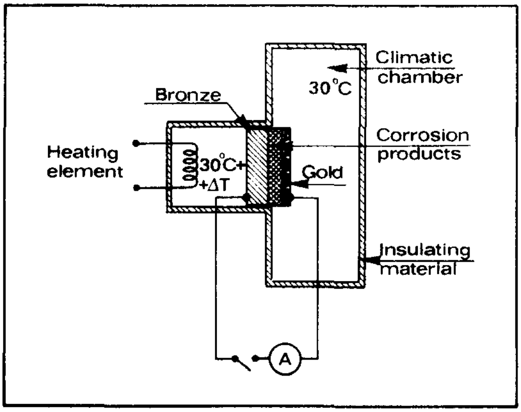

FIG. 5. Scheme of the method of overheating of the system of Fig. 1 with respect to r.t.

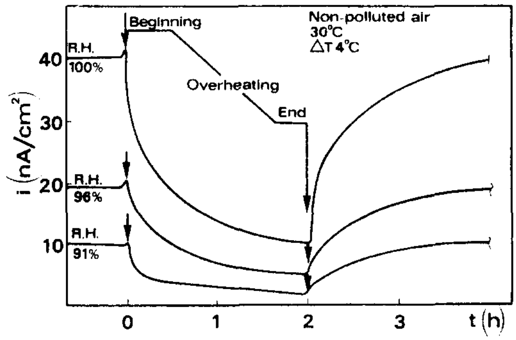

FIG. 6. Effect of the overheating on the short-circuit current of the system of Fig. 1, as a function of the time (t) after the beginning and the end of the overheating (ΔT 4°C) and of the r.h., in non-polluted air at 30°C.

TABLE 1. SHORT-CIRCUIT CURRENTS OF THE SYSTEM OF FIG. 1 MEASURED IN SOME TESTS OF DIRECT EXPOSURE TO THE URBAN–INDUSTRIAL ATMOSPHERE OF MILAN (THESE TESTS STARTED AT THE BEGINNING OF SEPTEMBER 1974)

Date (year, month, day, time)		Temperature (°C)	Relative humidity (%)	SO_2 content (ppm)	i(nA/cm²)			
					N.I.(a)	B(b)	M(c)	O.H.(d)
November 1974								
d	h							
18	17.30	9	94	0.06	0.5	<0.1	0.45	—
19	9.30(e)	8	85	0.10	260	39	83	—
	14.00	14	60	0.11	<0.1	<0.1	<0.1	—
January 1975								
d	h							
16	11.30	2	90	0.06	0.25	<0.1	0.35	—
17	13.00(e)	3	89	0.20	44	21	40	—
	15.30	3	89	0.24	6	4	6	1
	17.30	3	88	0.22	5	4	5	0.5
20	10.00	8	90	0.40	5	6	7	—
22	10.00	7	85	0.15	3	3	3	—
24	16.00	9	70	0.15	<0.1	0.35	<0.1	—
February 1975								
d	h							
4	10.00	6	60	0.11	<0.1	<0.1	<0.1	—
5	11.00(e)	3	88	0.24	10	4	7	—
6	9.30	2	91	0.27	8	5	8	—
13	11.30	8	83	0.22	8	4	8	—
17	10.00	7	60	0.06	<0.1	<0.1	<0.1	—

(a) Non-inhibited specimen
(b) Specimen treated with benzotriazole
(c) Specimen treated with 2-mercaptobenzothiazole
(d) Specimen overheated with respect to the ambient temperature (ΔT 4°C)
(e) Wet fog or damp smog.

In general, the correlation between relative humidity, sulphur dioxide content and short-circuit current of the system above described does not seem to be very good, owing to the following circumstances:

(i) the climatic data have not been recorded in the test site but they have been transmitted by the nearest weather-station in Milan;

(ii) the interference of the "ageing" effect (i.e. the formation of corrosion products in correspondence to the gold plate pores, which hinders the oxygen reduction process) and of the slow changes induced by the sulphur dioxide in the chemical composition of the preformed patina, with the consequent changes in the salts hygroscopicity (i.e. the main factor which instantaneously controls the short-circuit current), may complicate the response of the system.

Therefore, this very system is not fit for giving an instantaneous index of the environmental aggressiveness by means of the short-circuit current value. Nevertheless we think that a system of the type described above, suitably modified as far as the nature of the electrodes and of the corrosion products is concerned, could be effectively used as a sensor of the environmental aggressiveness. Experiments are proceeding in order to search into this point.

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