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EFFECTIVENESS OF SOME INHIBITORS ON THE ATMOSPHERIC CORROSION OF
GOLD PLATED BRONZES

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SUMMARY

The effect of some inhibitors (benzotriazole and 2-mercaptobenzothia
zole) on the atmospheric corrosion of gold plated bronzes has been
investigated.
The corrosion rate was determined by an electrochemical method which
allows its instantaneous values in the time to be followed. This
method is based on the measurement of the current flowing through a
model simulating the working conditions of gold plated bronzes in
the atmosphere (i.e.: bronze/corrosion products/porous gold film).
The action of these inhibitors has been evaluated in different con-
ditions of moisture and SO_2 content.

INTRODUCTION

In this paper some results concerning the effect of inhibitors on
the atmospheric corrosion of gold plated bronzes are given.
The investigation was carried out using a model of the real systems
set up in our laboratory (1) and consisting of a "sandwich" of bron-
ze 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 reprodu-
ce the corrosion phenomenon; the current thus measured by a null-re
sistance ammeter provides instantan eous and continuous information
on the corrosion rate of the bronze.
In effect the corrosion rate of the bronze is determined not only
by the operation of this galvanic cell, but also by the activity of
the local processes on the bronze. However, this latter activity, al
ready small in the absence of coupling with gold, is furthermore re-
duced by "differential effect" because of the coupling itself. There-
fore the corrosion current will be henceforth identified by us with
the short-circuit current of the system of fig. 1.
Being possible to measure currents of $10^{-9}A$, corrosion rates equal
to 1 mm/million of years on a specimen whose exposed area is 10 cm^2,
can be appreciated.
The idea of setting up the system above described evolved from the
studies carried out on the Paradise Door of the Baptistry at Floren
ce (2) and on the St.Marco Horses at Venice (2,3), which have shown
that there is often a layer of corrosion products between the gold
coating and the bronze below.

The aims of this research were the following ones :
i) to specify the influence on the corrosion rate of suitable
   corrosion inhibitors, in different working conditions as re-
   gards the relative humidity, the presence or not of liquid
   film on the gold coating, the presence of pollutants and their
   amount;
ii)to define the electrochemical aspects of the behaviour of the sy-
   stem so as to determine the type of kinetic control (i.e. anodic,
   cathodic or ohmic) of the overall corrosion process and the in-
   fluence of the corrosion inhibitors on the partial anodic and
   cathodic reactions.

EXPERIMENTAL

For the preparation of the specimens a suitably melted bronze ca-
sting of the following composition
83.90% Cu, 5.80% Sn, 4.25% Pb, 5.30% Zn, 0.58% Ni, traces of Fe,
was employed, from which disks 30 mm in diameter and 5 mm in thick-
ness were cut.
Vernon's (4) suggestions were followed for artificially forming the
patina of corrosion products, by anodically treating the bronze
for about 15 min. at a current density of 4 A/dm^2 in $MgSO_4$ (10% w/o)+
+$Mg(OH)_2$ (2%)+$KBrO_3$ (2%) aqueous solution at 95°C. A patina which is
very adherent to the base-metal is obtained with this procedure.
This film has an average thickness of about 70 μ and consists of
copper basic sulfates, which have compositions similar to the na-
turally formed ones analysed by Vernon.
The gold plates were prepared by deposition on an inert support,from
which they could be easily removed, by the vacuum evaporation tech-
nique (Edwards apparatus). The plates employed were about 20 μ thick.
Their porosity was determined by means of microscope observations
(Jeol scanning microscope U3) and of electrographic tests (Sel-Rex
Tester). A very large number of pores whose diameter was less than
one micron was found to be present, as well as small holes about
10 μ in diameter.
The gold plates were then fixed on the patinas of corrosion pro-
ducts with common glue spread around their edges.
The systems thus set up were inserted in the round seat of suitable
specimen holders (made of insulating material), where the electrical
connections are provided by flexible metallic tongs without danger
of damaging the gold plates (fig. 2).
The specimen holder was placed for operation in a cell at 30°C where
suitable saturated solutions provided controlled values of relative
humidity. Air for chromatographic use or alternatively air with
controlled SO_2 content (10 p.p.m.) was employed.
Also direct exposures of the systems to the urban-industrial atmo-
sphere of Milan were performed, in conditions which will be speci-
fied later on.
Before being utilized in the various experiments, the specimens we-
re allowed to operate short-circuited for some days in saturated at
mosphere, in order to reduce the irreproducibilities of behaviour

which appear particularly during the initial period.
2-mercaptobenzothiazole and benzotriazole were selected as corro-
sion inhibitors because of their acknowledged effectiveness towards
copper and its alloys, even the ancient bronzes covered with a na-
tural patina (5). In both cases the inhibiting treatment was perfor-
med by immerging separately the bronze disks covered with the arti-
ficial patina and the gold plates in absolute ethyl alcohol solu-
tion containing 3% of the considered inhibitor, at 60°C for 15 min.
The electrical equipment for the corrosion rates measurements consi-
sted of an Amel Mod. 668/RM null-resistance ammeter and of an Amel
Mod. 862/D recorder.
In order to specify the contributions to the voltage balance of the
system during its operation, a suitable bronze reference electrode
was introduced in the system itself through the bronze disk.
Polarization curves also were recorded separately for the anodic and
cathodic processes, i.e. respectively the dissolution of a bronze
electrode covered by its artificial patina and the oxygen reduction
on a gold electrode, both in the absence and in the presence of the
considered corrosion inhibitors, in a 0.2 M aqueous solution of
Na_2SO_4 at pH values of 5, 7 and 9.5, at a temperature of 25°C. In
the case of the anodic measurements the solution was deaerated by
circulation of nitrogen gas. In any case a Luggin-Haber capillary
probe and a Hg, Hg_2SO_4/K_2SO_4 (sat.) reference electrode were uti-
lized. The polarization curves were plotted by the potentiostatic
pulses method (each rectangular voltage pulse applied to the electro
de under study lasted 2 min. and its amplitude was increased by 5
or 10 mV each time; the interval between two successive pulses was
also of 2 min.). Amel equipment consisting of Mod. 551 potentiostat,
Mod. 560 interface and Mod. 862/D recorder was used for these measu-
rements.

RESULTS AND DISCUSSION

a) Corrosion Rate Measurements

The main results we have hitherto obtained are summarized in figu-
res 3 to 5.
For the system placed in non-polluted air (in particular in the
absence of SO_2) at relative humidity of 100% and in the presence
of condensed water on the surface of the gold plate, the corrosion
current had an order of magnitude of some hundreds of nA/cm^2 after
an exposure time of 24 hrs. At relative humidity of 100%, but with-
out apparent surface condensation, the corrosion current is of about
one order of magnitude lower, corresponding to some tens of nA/cm^2.
It further decreases sharply (fig. 3) together with the relative
humidity (the temperature being constant), falling to fractions of
nA/cm^2 at 60-70% of relative humidity (all these values refer to an
exposure time of 24 hrs.).
In any case, in the absence of SO_2 the corrosion current decreases

slowly but continuously in the time. For instance, after one month of operation, values of one order of magnitude lower than those referring to an exposure time of 24 hrs. were reached, and after three months the corrosion current became practically negligible even at 100% of relative humidity and in the presence of a liquid layer (fig. 3). As for this effect which occurs after long times of operation ("ageing" effect), it is essentially related to a separation of corrosion products (e.g. cuprous oxide) on the gold plate, which hinders the oxygen reduction process.

Again, in the absence of SO_2, the lowering effect on the corrosion rate produced by the selected corrosion inhibitors (2-mercaptobenzothiazole and benzotriazole) is very considerable for short exposure times, above all at the highest values of relative humidity and even in the presence of condensed water (fig. 4). Specifically in this latter case the corrosion current decreases from $\simeq 400$ nA/cm^2 to $\simeq 30$ nA/cm^2 by the benzotriazole treatment and to less than 10 nA/cm^2 by the 2-mercaptobenzothiazole one (exposure time 24 hrs.). In order to check the permanence of these beneficial effects, experiments have been carried out with the systems operating for longer times in distilled water. As a matter of fact, after ten days the corrosion current starts to increase and after ten more days it becomes of about one order of magnitude higher.

Some preliminary results in air with 10 p.p.m. SO_2(*) in the absence of condensed water are described in fig. 5. For short exposure times the corrosion current of the non-inhibited specimens is smaller than in non-polluted air (**) but, contrary to this latter case, there is no evidence, even after several days, of the "ageing" effect above mentioned, i.e. of the lowering in the time of the current itself (***), in relation to the non-separation of cuprous oxide on the gold plate. Furthermore the strong lessening of the influence on the corrosion rate in these conditions of the considered inhibitors must be pointed out. In the presence of condensed water on the surface of the gold plate, the corrosion current reaches again the order of magnitude of some hundreds of nA/cm^2 in the case of non-inhibited specimens and respectively of some tens of nA/cm^2 in the one of inhibited specimens (exposure time 24 hrs.).

(*)   A value which is very high even compared with strongly polluted atmospheres.

(**)   And it seems to remain small even if afterwards SO_2 is carefully removed from the measurement cell.

(***) So that after longer exposure times a reversed behaviour is found, i.e. the corrosion current in non-polluted air goes down below the values in the presence of SO_2.

At the end of this part it must be emphasized that the curves and the figures given above have a purely qualitative value and can change from one specimen to another because of the differences in porosity of the gold plates and the differences in contact area between the gold plates and the patinas underneath. Nevertheless the corrosion current always has the same order of magnitude for the different specimens, the working conditions being equal.

In the presence of SO_2 another source of error is connected with the difficulty of controlling at the same time the SO_2 content and the relative humidity of the atmosphere in the measurement cell by means of our discontinuous operating system. Nevertheless the given results are quite significant particularly as regards the comparison, under the same working conditions, between the non-inhibited specimens and the inhibited ones.

b) <u>Voltage and Overvoltage Measurements</u>

The voltage vs. time curves after the opening of the circuit show that the driving force available for the current circulation in the short-circuited system (which has an order of magnitude of 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 (which indicatively may be several ten times less than the above mentioned steady value of the open-circuit voltage). Ohmic-type control of the corrosion process can then be excluded.

On the other hand, the introduction in the system of a suitable bronze reference electrode shows that the anodic overvoltage also is negligible during the short-circuit operation. Therefore the overall corrosion process is cathodically controlled.

This result is confirmed by the relative steepness of the polarization curves of anodic dissolution of bronze covered by its artificially obtained corrosion products and of cathodic reduction of oxygen on gold in suitable solutions already reported (curves marked N.I. in figures 6 to 8). It may be seen in particular that the cathodic overvoltage increases by pH decreasing, as is well known.

Again, in figures 6 to 8, the curves marked M or B concerning the polarization measurements performed on specimens treated with the corrosion inhibitors above mentioned, show that these inhibitors essentially influence the cathodic process. Therefore this influence is falling by pH decreasing.

As a whole, the results of the overvoltage measurements appear to be consistent with those of the corrosion rate tests. In particular the low corrosion rates recorded in the presence of SO_2 in the given conditions may be related with the sluggish kinetics of the oxygen reduction process in acid medium.

c) Exposure to Urban-Industrial Atmosphere

Results concerning some tests of direct exposure of the system
to the urban-industrial atmosphere of Milan are summarized in tab.1.
These tests started at the beginning of september 1974.
From a qualitative point of view, the following trends stated above
are confirmed :
i) in the presence of SO_2 and other pollutants, the lowering effect
on the corrosion rate caused by the "ageing" of the system during
its operation vanishes;
ii) in the same conditions, the influence on the corrosion rate of
the considered inhibitors vanishes too. As a matter of fact, in
november 1974 the non-inhibited specimens and the inhibited ones
showed a different behaviour in strongly aggressive conditions, but
subsequently every difference disappeared.
On the contray, the relation between the figures given in tab. 1
and the laboratory results is less evident from a quantitative
point of view, particularly as regards the influence of the SO_2 con-
tent of the atmosphere (*). As a matter of fact, the amount of SO_2
or of other pollutants fixed on the specimen surface seems to be a
more significant factor, as is shown by the peaks in the corrosion
current (up to about one hundred nA/cm^2) recorded, even in the pre-
sence of corrosion inhibitors, in correspondence to "thermic inver-
sion" conditions with damp smog. In the absence of damp smog, the
corrosion rate becomes appreciable if both the SO_2 content and the
relative humidity of the atmosphere simultaneously exceed certain
threshold values.
In this connection it is wortwhile mentioning that the system set up
could be effectively used to define an index of the environmental ag-
gressiveness and of its time variations, by means of the short-
circuit current values.

At the end of this paper it must be emphasized that much work has to
be further carried out in order to go deeply into the understanding
of the complex phenomena which occur in the considered corrosion sy-
stems.

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    dings 29th Meeting Associazione Termotecnica Italiana, Florence,
    Sept. 1974, in the press.
(2) M. Leoni: Met. Ital., Atti Notizie 27, 157 (1972).
(3) B. Bearzi : Met. Ital., Atti Notizie 20, 203 (1965).

(*) In the case of direct exposure to the urban-industrial atmosphere,
    also the influence of other pollutants must be taken into account,
    with possible synergy-effects.

(4) W.H.J. Vernon: J. Inst. Metals 49, 153 (1932); W.H.J. Vernon, L. Whitby: ibidem 44, 389 (1930) and 42,181 (1929).

(5) P.A. Borea, G. Gilli, G. Trabanelli, F. Zucchi : Proceedings 3rd European Symposium on Corrosion Inhibitors, Ferrara, Sept. 1970, Università degli Studi di Ferrara (1971), p.893; G. Trabanelli, F. Zucchi: Met. Ital., Atti Notizie 29, 505 (1974); I. Dugdale, J.B. Cotton: Corrosion Sci. 3, 69 (1963).

Tab. 1 — Short-circuit currents of the system of fig. 1 in some tests of direct exposure to the urban-industrial atmosphere of Milan.

Date (year,month,day,time)	Temperature (°C)	Relative humidity (%)	SO_2 content (p.p.m.)	$i(nA/cm^2)$		
				N.I.(a)	B(b)	M(c)
November 1974						
d. hrs.						
18 17.30	9	94	0.06	0.5	<0.1	0.45
19 9.30(d)	8	85	0.10	260	39	83
14.00	14	60	0.11	<0.1	<0.1	<0.1
January 1975						
d. hrs.						
16 11.30	2	90	0.06	0.25	<0.1	0.35
17 13.00 (d)	3	89	0.20	44	21	40
15.30	3	89	0.24	6	4	6
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. hrs.						
4 10.00	6	60	0.11	<0.1	<0.1	<0.1
5 11.00	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) Damp smog
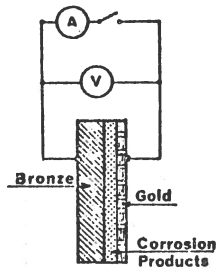
Fig. 1 - Scheme of the artificially set up corrosion system :
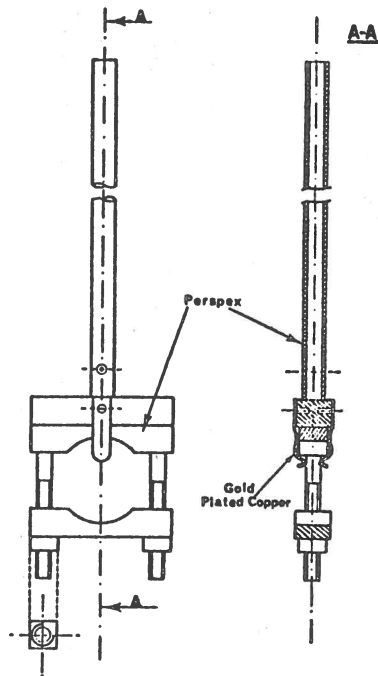bronze/corrosion products/porous gold plate.
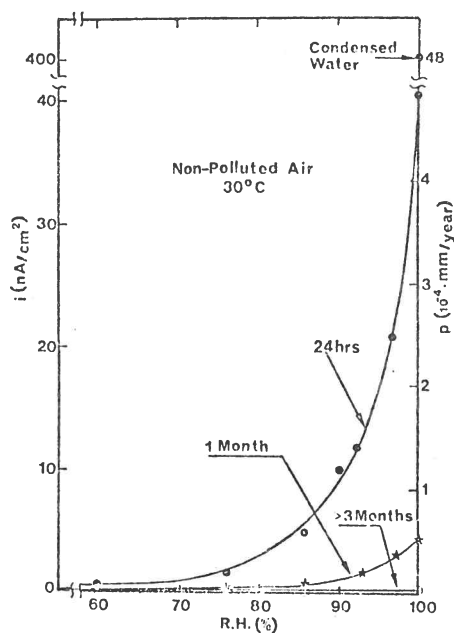

Fig. 2 - Specimen holder.

Fig. 3 — Short-circuit current of the system of fig.1, as a function of the relative humidity (R.H.) and 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).
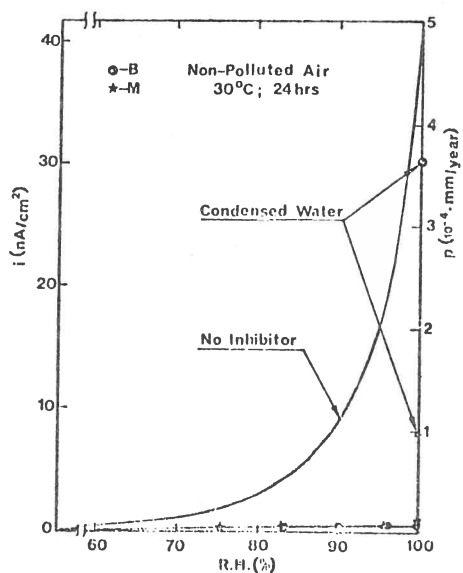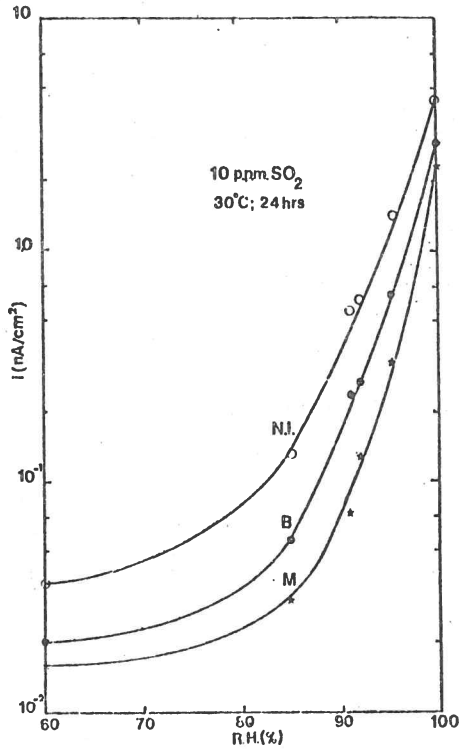

Fig. 4 — Effect of the corrosion inhibitors: 2-mercaptobenzothiazole (M) and benzotriazole (B) on the short-circuit current of the system of fig. 1, as a function of the relative humidity (R.H.) in non-polluted air at 30°C, for an exposure time of 24 hrs. On the right hand ordinate axis, current density (i) values are converted into penetration rates (p).

Fig. 5 - Effect of the corrosion inhibitors: 2-mercaptobenzothiazole (M) and benzotriazole (B) on the short-circuit current of the system of fig. 1, as a function of the relative humidity (R.H.) in air with 10 p.p.m. SO_2 at 30°C, for an exposure time of 24 hrs. N.I. = non-inhibited specimen.
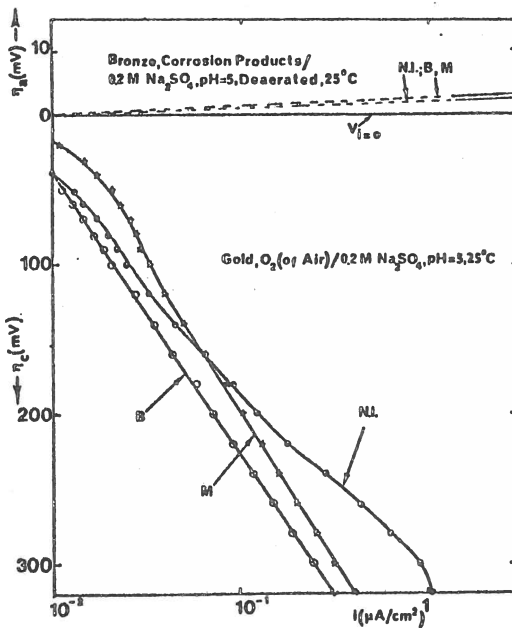

Fig. 6 - Overvoltage (η) vs. current density (i) curves for the systems: bronze, corrosion products/ 0.2 M Na_2SO_4 deaerated solution, pH 5 (anodic curves) and : gold, O_2 (of air)/0.2 M Na_2SO_4 solution, pH 5 (cathodic curves), at 25°C. N.I. = non-inhibited specimen; B= specimen treated with benzotriazole; M = specimen treated with 2-mercaptobenzothiazole.
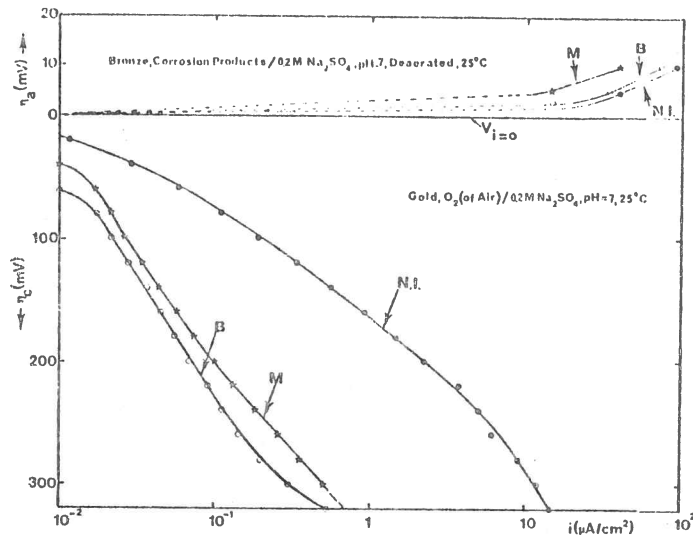
Fig. 7 — Overvoltage (η) vs. current density (i) curves for the systems: bronze, corrosion products/0.2 M Na$_2$SO$_4$ deaerated solution, pH 7 (anodic curves) and: gold, O$_2$ (of air)/0.2 M Na$_2$ SO$_4$ solution, pH 7 (cathodic curves), at 25°C. N.I. = non-inhibited specimen; B = specimen treated with benzotriazole; M = specimen treated with 2-mercaptobenzothiazole.
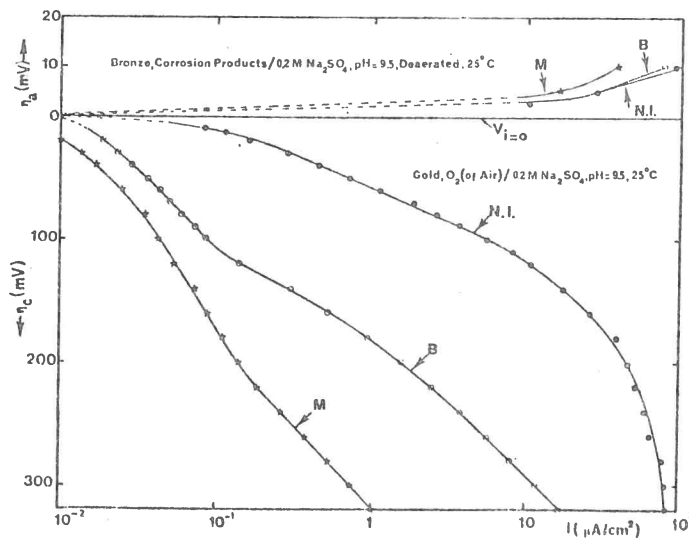

Fig. 8 — Overvoltage (η) vs. current density (i) curves for the systems: bronze, corrosion products/ 0.2 M Na$_2$SO$_4$ deaerated solution, pH 9.5 (anodic curves) and : gold, O$_2$ (of air)/0.2 M Na$_2$SO$_4$ solution, pH 9.5 (cathodic curves), at 25°C. N.I. = non-inhibited specimen; B = specimen treated with benzotriazole; M = specimen treated with 2-mercaptobenzothiazole.