Atmospheric corrosion inhibitors for copper in the electronics industry

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Inhibiting efficiencies of various imidazole derivatives on atmospheric corrosion of copper on printed circuit boards were investigated. Experiments were carried out on double sided copper boards using a procedure based on international standards and applied in the electronics industry. Electrochemical measurements were performed on copper in solutions containing imidazole derivatives, under stationary and flow conditions. The influence of flow velocity and temperature on the inhibiting characteristics was investigated. The imidazole derivatives studied have good inhibiting properties for copper against atmospheric corrosion.

List of symbols

b_a, b_c Tafel coefficients (anodic and cathodic) (mV)
d cell diameter (m)
E_a activation energy (J mol^{-1})
E_{corr} corrosion potential (mV)
j_{corr} corrosion current density (mA cm^{-2})

μ electrolyte viscosity (Pa s)
Q throughflow (dm^3 min^{-1})
ρ electrolyte density (kg m^{-3})
Re Reynolds number
v electrolyte velocity (m s^{-1})
v_{corr} corrosion rate (mm y^{-1})

1. Introduction

Copper is commonly used in microelectronics and may be susceptible to atmospheric corrosion during both storage and use of the device. Atmospheric corrosion of copper can bring about significant problems in terms of microelectronic interconnections and solderability of electronic components onto copper layers in printed circuit boards.

Inhibitors are now widely used in industry to prevent corrosion of copper when exposed to both atmospheric and immersed conditions. Benzotriazole (BTA) and its derivatives are currently in use for both atmospheric copper corrosion protection and aqueous phase protection [1–26]. However, a very important deficiency of BTA and BTA-derivatives is their toxicity [27]. Thus, their replacement by new environment-friendly inhibitors is desirable.

The aim of this work is to study the efficiency of imidazole derivatives as atmospheric corrosion inhibitors for copper in the electronics industry and, in particular, in technological processes used in printed circuit-board production. Now, industrial plants frequently handle flowing media. Flow can enhance general corrosion rates and initiate, or prevent, localized attack on materials, depending on the type of

corrosion and of flow rate [28]. It is known that corrosion inhibitors may loose their effectiveness above a critical flow rate which depends on the nature and molecular structure of the inhibitor as well as its concentration. Therefore, this electrochemical study of the effectiveness of copper corrosion inhibitors has been undertaken under both stationary and flow regimes.

2. Experimental details

The following organic compounds were studied as atmospheric corrosion inhibitors for copper: 5-hydroxymethyl–4-methylimidazole (**1**): 5-hydroxymethyl–4-methylimidazole hydrochloride (**2**); and ethyl–4-methyl–5-imidazolecarboxylate (**3**). The efficiency values obtained were compared with those for benzotriazole-based commercial inhibitor for copper (Entek Cu 56 supplied by Enthone–OMI) under the same conditions.

The experiments were carried out on double sided copper boards, using a procedure that complies with electronics industry rules based on international standards (DIN, SIS, IEC). Copper panels were degreased in organic solvent, rinsed in deionized water, immersed in microetching solution (H_2SO_4 + H_2O_2) for 60 s at 35 °C, and rinsed in deionized water. The

panels were than immersed, at room temperature, in the inhibitor solution and, after 60 s, they were rinsed in deionized water and dried in warm air. The appearance of protected panels was light pink and the surface was free from spots. The inhibitor protects the copper surface against atmospheric oxidation during storage, transport and handling.

The protection efficiency of inhibitor layers applied on panels was tested by means of a nitric acid test and a solderability test. These two methods were applied prior to, and after, copper panels had been submitted to an accelerated ageing test in a humidity chamber.

2.1. Nitric acid test

The aim of the nitric acid test was to test the quality of copper protection by the inhibitor coating. A drop of 10% nitric acid was placed on the treated copper surface. The drop should not spread and no bubbling should occur for at least 60 s. The appearance of the drop was then examined under light and magnification. The development of hydrogen bubbles, caused by copper corrosion, indicates the quality of inhibitor protection. If no bubbles appear on the copper surface within 60 s then the quality of the inhibitor coating is considered satisfactory.

2.2. Solderability test

The purpose of this test was to determine the solderability of printed circuit boards that are to be joined by a soldering. The method of testing complies with IEC 326-2 and indicates the resistance of inhibitor-protected copper surfaces to atmospheric corrosion. The solderability test was carried out in molten solder alloy (60% tin and 40% lead) at 260 °C for 5 s. The solderability of copper panels was examined visually. A smooth, bright, easily wetted copper surface indicates good solderability of copper samples submitted to testing. In the case of low inhibitor efficiency, the copper surface becomes oxidized under atmospheric conditions and the solderability test results in severe dewetting and nonwetting of the copper surface.

2.3. Humidity chamber

The environmental testing is an important part of the development and qualification process for electronic devices and is increasingly used to ensure high reliability of circuit boards and assemblies. Temperature–humidity cycling tests are used to ensure that electronic equipment will withstand environmental condition during storage and installation, as well as during the working life of such devices [29].

The accelerated ageing test was performed on passivated copper samples in a humidity chamber. Such chambers provide a wide range of possibilities for the accelerated atmospheric corrosion testing because microclimate conditions, such as temperature and relative humidity, can be varied. Two 24-hour

cycles were applied. At the beginning of each cycle the temperature was increased from 25 to 55 °C for 2 h while the relative humidity was 80–100%. The temperature was maintained at 55 °C for 16 h with relative humidity of 95–100%. The chamber was then cooled to 25 °C for 6 h. After testing, the samples were inspected visually and evaluated in accordance with relevant requirements. The nitric acid and solderability tests were carried out before and after the accelerated corrosion test, as previously described.

2.4. Electrochemical measurements

Electrochemical measurements on copper were performed under stationary and flow conditions. The flow-through cell ($V = 0.5$ dm^3) with thermometer and three electrodes (working electrode, reference electrode and auxiliary electrode) (Figs 1 and 2) was linked to a flowmeter ($Q = 0.4$–4.0 dm^3 min^{-1}), pump ($Q = 21$ dm^3 min^{-1}), vessel (2.5 dm^3) and valves. Electrodes were connected to a Wenking 72 potentiostat. The experiments were performed at a flow rate of $v_1 = 0.005$ m s^{-1} and $v_2 = 0.015$ m s^{-1}. The Reynolds number was calculated according to the relation:

$$Re = vd\rho/\mu$$

where v is the electrolyte velocity (m s^{-1}), d the cell diameter (m), ρ the electrolyte density (10^3 kg m^{-3}) and μ-electrolyte viscosity (10^3 Pa s).
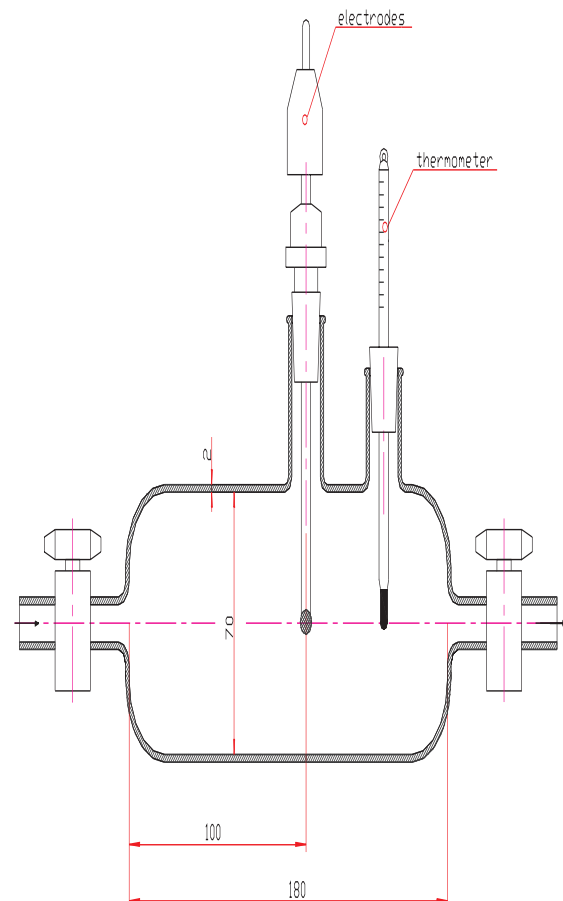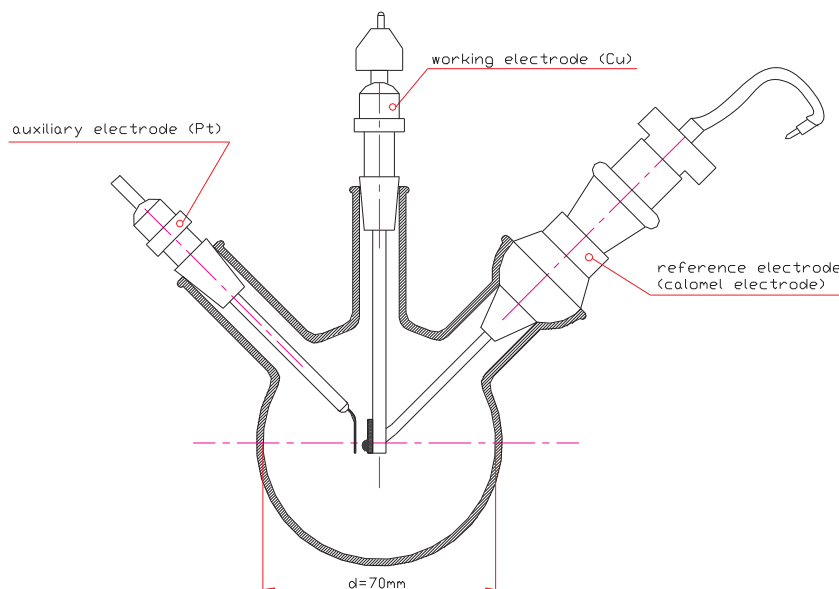

Fig. 1. Longitudinal section of the cell.

Fig. 2. Cross section of the cell.

The Reynolds number values ($Re_1 = 361$ and $Re_2 = 1086$) confirm that experiments were performed under conditions of laminar flow.

Electrochemical experiments were carried out using a working electrode of polycrystalline copper rod (99.98%), in solutions containing imidazole derivatives and benzotriazole-based commercial inhibitor in various concentrations (0.1%, 1%, 1.5%, 2.0% and 2.5%).

The copper electrode surface was abraded with emery paper to a 4000 metallographic finish, polished with Al_2O_3 ($\delta = 0.01–0.3\ \mu m$) to a mirror finish, degreased in ethanol and rinsed with redistilled water. In all measurements the counter electrode was a platinum electrode and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary. All potentials are referred to the SCE scale. The corrosion current densities were determined using the Tafel extrapolation method. Measurements were performed in the temperature range of 20 to 45 °C.

3. Results

3.1. Study of atmospheric corrosion

Results indicating inhibiting efficiency of imidazole derivatives with respect to atmospheric corrosion of copper (solderability test and HNO_3-test) before and after the accelerated corrosion in humidity chamber are presented in Table 1. For comparison purposes, the study also included analysis of the Entek Cu 56

Table 1. The results of the investigation of copper atmospheric corrosion inhibitors (solderability test and HNO_3-test) before and after the humidity chamber

Inhibitor		Before humidity chamber		After humidity chamber	
		Solderability test	HNO_3-test	Solderability test	HNO_3-test
Inhibitor 1	(1.0%)	+	+	+	+
	(1.5%)	+	+	+	+
	(2.0%)	+	+	+	+
	(2.5%)	+	+	+	+
Inhibitor 2	(1.0%)	+	+	+	−
	(1.5%)	+	+	+	+
	(2.0%)	+	+	+	+
	(2.5%)	+	+	+	+
Inhibitor 3	(0.1%)	+	−	+	−
Inhibitor 4	(1.0%)	+	+	+	+
	(1.5%)	+	+	+	+
	(2.0%)	+	+	+	+
	(2.5%)	+	+	+	+

Legend:
Inhibitor 1 (**1**)
Inhibitor 2 (**2**)
Inhibitor 3 (**3**)
Inhibitor 4 Entek Cu 56 (benzotriazole)

(benzotriazole) which is a commercial inhibitor for copper.

3.2. *Electrochemical measurements*

Potentiostatic polarization curves for copper in 1% (**1**) at various flow rates ($v_1 = 0$ m s^{-1}, $v_2 = 0.005$ m s^{-1} and $v_3 = 0.015$ m s^{-1}) at 20 °C, without ohmic correction, are presented in Fig. 1. Anodic and cathodic Tafel lines for copper in 1% (**1**) at 38 °C at various flow rates are presented in Fig. 2.

Fig. 3 shows dependence of the corrosion current density on flow rate at various temperatures (20–45 °C).

The determination of the apparent activation energy, E_a, for copper in 1% (**1**) at different flow rates ($v_1 = 0.005$ m s^{-1} and $v_2 = 0.015$ m s^{-1}) is presented in Fig. 4. Table 2. shows the corrosion parameters (E_{corr}, j_{corr}, b_a and b_c) for copper in 1% (**1**) at various temperatures and for different flow rates.

The general dependence of the corrosion rate, v_{corr} on the flow velocity, v, is established in accordance with the following relation:

$$v_{corr} \approx v^c \qquad (1)$$

In the following relationship, v_{corr} is calculated with j_{corr} taking at that into account the copper-dissolution valence, the atomic mass of copper and the copper density:

$$v_{corr}/\text{mm y}^{-1} = 11.6 \times 10^3 j_{corr}/\text{A cm}^{-2}$$

The exponent c depends on the flow regime; c is closer to the lower value in case of laminar flow, while it is closer to the higher value in the case of turbulent flow. Table 3 presents the dependence of the exponent c on the temperature and flow velocity.

4. Discussion

Imidazoles are heterocyclic organic compounds with three carbon and two nitrogen atoms in the ring. One of the nitrogen atoms is of pyrrole type and the other is a pyridine-like nitrogen atom. The imidazole molecule shows three different anchoring sites that are suitable for surface bonding: the nitrogen atom with its lone sp^2 electron pair, the C(4)H–C(5)H–'edge' and the aromatic ring [30]. Imidazoles are therefore potentially effective inhibitors. The efficiency of some imidazole derivatives when used for copper and its alloys [11, 31–33] as well as for iron [34–38] was established. In contrast to benzotriazole, imidazoles are not toxic.

Inhibiting efficiencies of studied imidazole derivatives were compared with the efficiency value of Entek Cu 56 (benzotriazole), a commercially-available inhibitor for copper.

Results obtained by the solderability test and HNO$_3$ test before and after the humidity chamber show that imidazole derivatives – when used in the same concentrations as commercial inhibitors – present good inhibiting properties. The best inhibiting properties are attributed to (**1**) which is effective in the entire concentration range between 1.0% and 2.5%. (**3**) was, by reason of low solubility, investigated only in concentration of 0.1%; this provided poor results during HNO$_3$ test conducted before and after humidity chamber. All investigated inhibitors showed good solderability before and after humidity chamber.
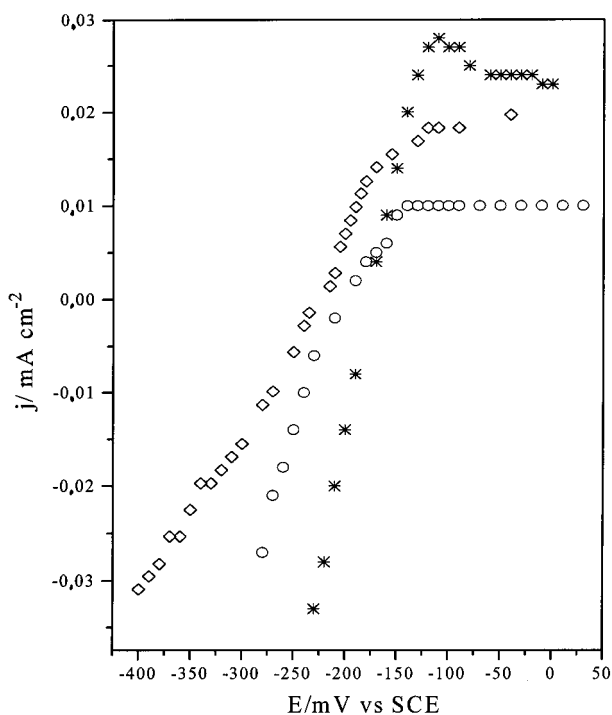

Fig. 3. Potentiostatic polarization curves for copper in 1% (**1**) at various flow rates: $v_1 = 0$ m s^{-1} ($\diamond$), $v_2 = 0.005$ m s^{-1} ($\circ$) and $v_3 = 0.015$ m s^{-1} ($*$) at 20 °C.
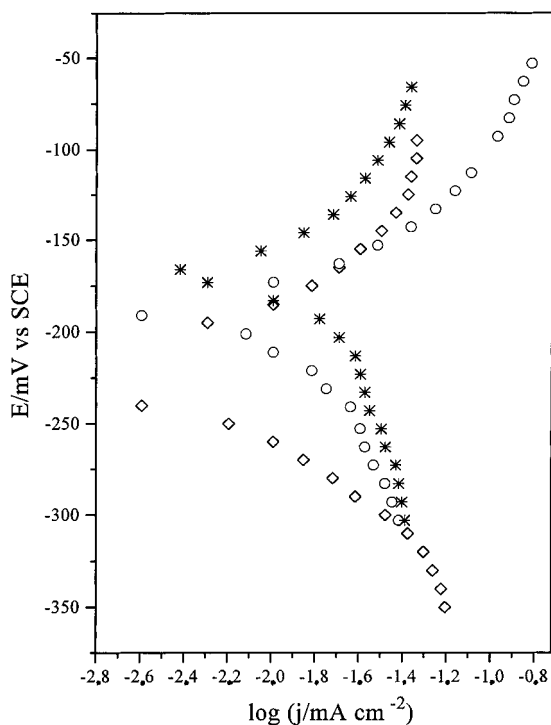
Fig. 4. Anodic and cathodic Tafel lines for copper in 1% (**1**) at $v_1 = 0$ m s^{-1} ($\diamond$), $v_2 = 0.005$ m s^{-1} ($\circ$) and $v_3 = 0.015$ m s^{-1} ($*$) at 38 °C.

*Table 2. Kinetic parameters for copper in 1% (**1**) at various temperatures and for different flow rate*

Temperature, T /°C	Throughflow, Q /dm³ min⁻¹	Velocity, v /m s⁻¹	E_{corr} /mV	j_{corr} /mA cm⁻²	b_a /mV	b_c /mV
20	0	0	−220	0.001	35	50
	1.2	0.005	−190	0.002	30	100
	3.6	0.015	−175	0.006	70	90
30	0	0	−225	0.003	75	100
	1.2	0.005	−160	0.005	80	50
	3.6	0.015	−145	0.008	100	50
38	0	0	−210	0.002	40	60
	1.2	0.005	−190	0.006	50	100
	3.6	0.015	−170	0.010	100	90
45	0	0	−260	0.006	80	50
	1.2	0.005	−190	0.010	60	90
	3.6	0.015	−170	0.012	80	110

To gain a better insight into processes occurring at the copper-inhibitor solution interface, the corresponding electrochemical measurements were performed on copper in imidazole-derivative solutions. The investigation was performed under both stationary and flow regimes.

The electrochemical investigation in the temperature range between 20 °C and 45 °C at a laminar flow regime ($Re < 2000$) indicates that the corrosion current density increases with an increase in temperature as well as with an increase in flow velocity. This is in accordance with the value of activation energy which depends on the velocity of flow. Activation-energy values for 1% (**1**) are:

$$E_{a_1} = 21.5 \text{ kJ mol}^{-1} \text{ for the flow rate of}$$
$$v_1 = 0.005 \text{ m s}^{-1}$$

$$E_{a_2} = 7.7 \text{ kJ mol}^{-1} \text{ for the flow rate of}$$
$$v_2 = 0.015 \text{ m s}^{-1}$$

The exponent c, calculated according to Relation 1, decreases with temperature and increases with flow velocity, and ranges between 0.407 and 0.633 depending on the temperature and flow velocity (Table 3). This is in accordance with the data given in [28] where the exponent c ranges between 0.3 and 1, depending on the flow regime; c is closer to the lower value in the case of lower flow velocity. During the study of chemical

Table 3. Dependence of the exponent 'c' upon the temperature and flow velocity

T/°C	v/m s⁻¹	c
20	0.005	0.610
20	0.015	0.633
30	0.005	0.538
30	0.015	0.566
38	0.005	0.502
38	0.015	0.513
45	0.005	0.407
45	0.015	0.470

reaction between imidazole and metallic copper by i.r. and X-ray photoelectroscopy, Xue *et al.* [26] found that the di-imidazolatocopper (II) complex forms on the chemically cleaned copper surface.

Di-imidazolatocopper (II) is unsoluble in common solvents and is generally considered to be polymeric in nature. When a copper disc was immersed in imidazole solution a di-imidazolatocopper (II) polymeric film formed on the surface of copper as a corrosion-inhibiting layer.

5. Conclusion

(i) The inhibiting efficiency of imidazole derivatives (**1–3**) as atmospheric corrosion inhibitors of copper was studied and compared with the efficiency of a commercially-available benzotriazole-based inhibitor.
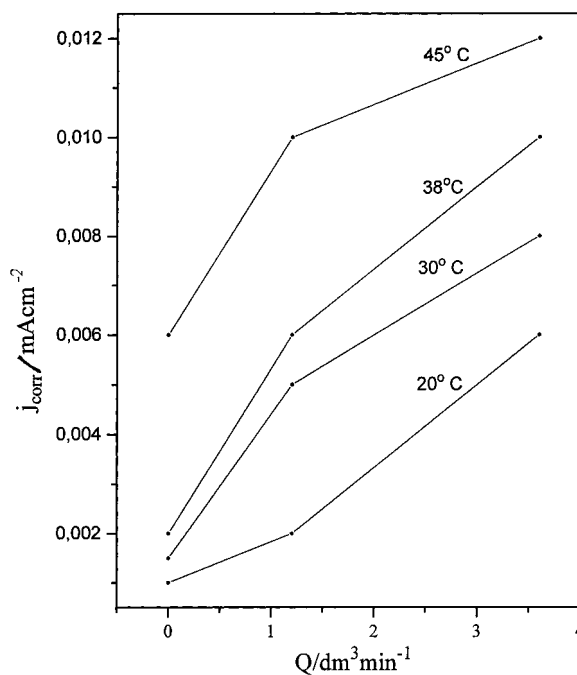

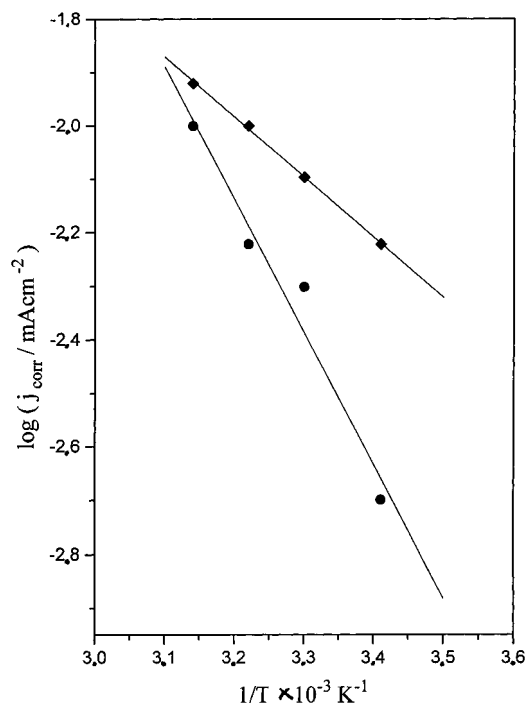Fig. 5. Dependence of corrosion current density upon flow rate at various temperatures (20–45 °C).

Fig. 6. Determination of activation energy E_a for copper in 1% (**1**) at flow rates $v_1 = 0.005$ m s^{-1} (○) and $v_2 = 0.015$ m s^{-1} (*).

(ii) The results of testing undertaken (solderability test and HNO$_3$-test) before and after accelerated corrosion in humidity chamber indicate that all investigated compounds present good inhibiting characteristics for atmospheric copper corrosion with the exception of (**3**) which was, by reason of low solubility, investigated only in concentration of 0.1%.

(iii) Electrochemical measurements in the temperature range between 20 °C and 45 °C at a laminar flow regime show that corrosion rate increases with an increase in temperature as well as with an increase in flow velocity.

(iv) Activation energy values for copper in the solution containing imidazole derivatives decrease with an increase in flow velocity.

Acknowledgement

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