Copper Corrosion Inhibition In Printed Circuit Board Production

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The inhibiting efficiency of imidazole derivatives (4-methyl-5-hydroxymethylimidazole and 1-butyl-5-methylimidazole) on atmospheric corrosion of copper in printed circuit board production was investigated. The experiments were carried out on single-sided copper boards, using a procedure based on standards applied in the electronic industry. The electrochemical investigation based on potentiodynamic polarization (Tafel extrapolation and polarization resistance measurements) on copper in the solutions used was performed at various temperatures (25 to 55 °C). The results obtained were compared with the efficiency of a commercial inhibitor for copper.

In-process corrosion and resultant yield loss are a costly problem for electronic components. These components are exposed to a range of uncontrolled environments, and for these and other reasons, understanding and control of corrosion in electronics is a challenging field that will face increasing demands as the technologies advance.[1]

On–chip metal lines provide local interconnection to join a cluster of elements and provide power to the elements.[2] The most used conductor material is copper that may be exposed to aggressive environments. Corrosion of ICs during processing can be a costly problem.[1]

The application of inhibitors is common in the electronics industry for prevention of corrosion of copper under atmospheric conditions and to preserve the solderability of the copper surface on boards. To provide good solderability of copper and electronic components onto the printed circuit boards, formation of corrosion products on copper must be avoided. The products of copper corrosion adversely influence the solderability of copper and the wettability of the copper surface with solder alloy. For protection against atmospheric corrosion and to maintain solderability of copper, the use of organic inhibitors is increasing. In the soldering process, acid flux dissolves the inhibitor coating very quickly and makes the copper surface active.

The aim of this research was to study the efficiency of imidazole derivatives as atmospheric corrosion inhibitors for copper in printed circuit board production.

Experimental Procedure

The inhibiting efficiency of 4-methyl-5-hydroxymethylimidazole and 1-butyl-5-methylimidazole on atmospheric corrosion of copper in printed circuit board production was studied. The efficiency values obtained were compared with those of a commercial inhibitor for copper[a] under the same conditions. Because the commercial inhibitor contained various heterocyclic organic compounds in 5-pct formic acid, the inhibitors mentioned were also investigated in 5-pct formic acid. The mass concentrations of the imidazole derivatives were 0.5, 1.0, 1.5 and 2.0 percent. The experiments were carried out on single-sided copper boards, and the procedure complied with the rules based on international standard IEC 326-2.

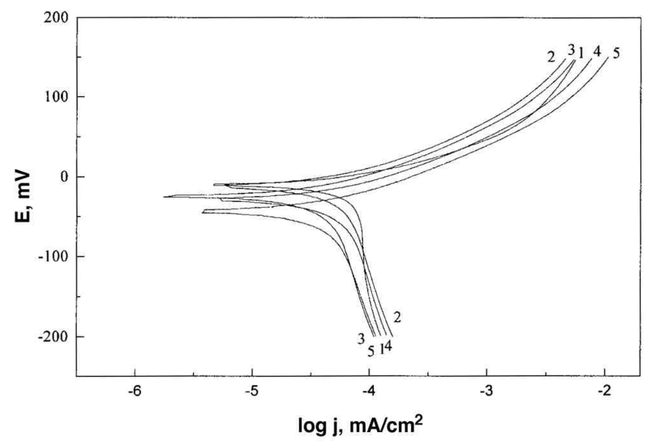

Fig. 1—Anodic and cathodic Tafel lines for copper in 5% HCOOH (1) and with addition of 4-methyl-5-hydroxymethylimidazole at concentrations of: 0.5% (2), 1% (3), 1.5% (4) and 2% (5) at 25 °C.

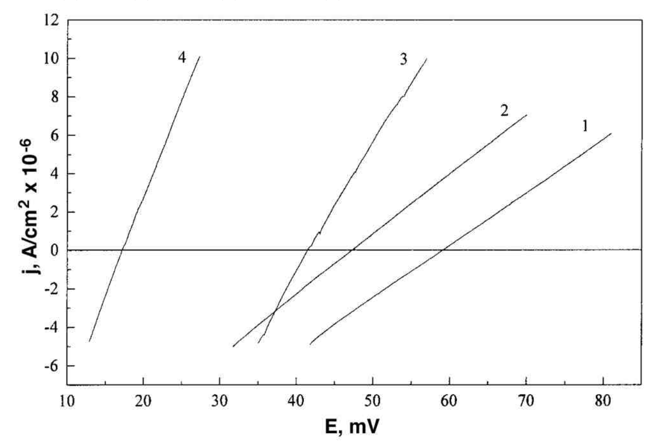

Fig. 2—Linear polarization curves for copper in solution of commercial inhibitor at 25 °C (1), 35 °C (2), 45 °C (3) and 55 °C (4).

Cleaning and activation of copper surfaces were provided by immersion in a 30-pct solution of cleaner[b] at 45 to 50 °C for 3 to 5 min. Microetching removes oxide layers and ensures bright, clean and uniform micro-roughness on the surface of the copper boards. The solution was prepared by dissolution of 90 to 120 g/dm^3 of a commercial etch[c] in 1- to 2-pct sulfuric acid for 1 to 2 min at 20 to 30 °C.

Microetching was followed by etching in sulfuric acid (mass concentration 90 to 120 g/dm^3) for one min at room temperature. After each treatment, the copper panels were rinsed in deionized water to remove remainder chemicals.

[a]*Entek Plus Cu-106 A, Enthone-OMI Ltd., Surrey, England*
[b]*Entek Cleaner SC-1010, Enthone-OMI Ltd.*
[c]*Entek Micro Etch ME-1020, Enthone-OMI Ltd.*
[d]*PARC 263 A*
[e]*PARC Model 352/252 SoftCorr.*

Table 1
Solderability & HNO_3 Tests Before & After Humidity Tests

Inhibitor	Before Humidity Tests		After Humidity Tests	
	Solderability	HNO_3	Solderability	HNO_3
1. (25 °C)	+	+	+	+
2. (25 °C)	+	-	+	+
3. (25 °C)	+	+	+	+
3. (35 °C)	+	+	+	+
3. (45 °C)	+	+	=	+
3. (55 °C)	+	+	+	+

(+) pass (-) fail
Inh. 1: 4-methyl-5-hydroxymethylimidazole
Inh. 2: 1-butyl-5-methylimidazole
Inh. 3: Commercial

Table 2
Inhibitor Layer Thickness (D) of 4-methyl-5-hydroxymethylimidazole & Commercial Inhibitor at Copper Surface at Different Temperatures D, μm

Inhibitor	25 °C	35 °C	45 °C	55 °C
1.	0.2	0.4	0.4	0.4
2.	0.2	0.3	0.3	0.3

Inh. 1: 4-methyl-5-hydroxymethylimidazole
Inh. 2: Commercial

Table 3
Corrosion Parameters for Copper Obtained by Tafel Extrapolation 25 °C

		$E_{corr(SCE)}$ mV	j_{corr} μA/cm²	b_a mV	$-b_c$ mV	CR mm/yr	z %
5% HCOOH		-10.35	21.01	23.58	33.38	0.514	–
Inh. 1	(0.5%)	-27.37	8.126	19.39	30.48	0.199	61
	(1.0%)	-27.78	6.710	18.92	26.67	0.164	68
	(2.0%)	-41.66	7.969	22.00	33.49	0.195	62
Inh. 2	(0.5%)	-12.39	12.49	24.00	30.97	0.305	41
	(1.0%)	-24.48	7.536	18.60	23.45	0.18	64
	(1.5%)	-28.67	11.05	19.04	30.55	0.27	47
	(2.0%)	-43.45	11.31	22.66	40.90	0.276	46
Inh. 3		42.47	1.671	50.17	52.44	0.041	92

Inh. 1: 4-methyl-5-hydroxymethylimidazole
Inh. 2: 1-butyl-5-methylimidazole
Inh. 3: Commercial

The panels were then immersed in the inhibitor for 60 sec at room temperature, dried for two min in air, then rinsed in deionized water and dried in warm air. The inhibitor protects the copper surface against atmospheric corrosion during storage, transport and handling.

The protective efficiency of inhibitors was tested by means of the following methods:

1. Nitric acid test
2. Solderability test

Nitric Acid Test: A drop of 10-pct nitric acid is placed on the treated copper surface. If no bubbles appear on the copper surface within 60 sec, the quality of the inhibitor coating is considered satisfactory.

Solderability Test: This test is carried out in molten 60/40 solder alloy at 260 °C for five sec. A smooth, bright, easily wetted copper surface indicates good solderability of copper samples and a well-protected surface.

These two methods were applied before and after accelerated aging tests on copper panels in a humidity chamber. The procedure for these tests is described in more detail elsewhere.[3]

Inhibitor layer thickness was determined using UV spectrophotometry by measuring the absorbance of the solution obtained by dissolution of inhibitor layers in hydrochloric acid. The procedure is designed to measure the thickness of the corrosion inhibitor film deposited by a commercial inhibitor.[4]

The electrochemical experiments were carried out in a classic electrolytic cell with the working electrode made from polycrystalline copper rod (99.98%), insulated with polytetrafluoroethylene (PTFE) tape, such that the area exposed to solution was 0.785 cm². The counter-electrode was a platinum plate and the reference was a saturated calomel electrode (SCE). All potentials were refereed to the SCE scale. Potentiodynamic measurements were conducted using a potentiostat/galvanostat[d] and controlled with corrosion analysis software.[e]

The corrosion current densities were determined by Tafel extrapolation and polarization resistance measurements, described earlier.[5]

Results

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

The results of the atmospheric corrosion tests of copper show that imidazole derivatives have good inhibiting efficiency similar to the commercial inhibitor, except the HNO_3 test before the accelerated corrosion test in the humidity chamber. The results of the inhibitor layer thickness determination (D) calculated before and after the humidity chamber are listed in Table 2.

The values of the layer thickness of 1-butyl-5-methylimidazole could not be determined because of turbidity of the solution, especially at higher temperatures. The layer of 4-methyl-5-hydroxymethylimidazole is somewhat thicker than those of commercial inhibitors in the whole range of temperatures investigated.

Figure 1 shows anodic and cathodic Tafel lines for copper in 5-pct HCOOH and with the addition of 4-methyl-5-hydroxymethylimidazole at different concentrations at 25 °C. Corrosion parameters and protection degrees for copper in the tested solutions at 25 °C and obtained by Tafel extrapolation are presented in Table 3. Figure 2 shows polarization resistance determination using linear polarization of copper in the solution of the commercial inhibitor. Corrosion parameters for copper in 0.5 M HCOOH, with addition of the imidazole derivatives obtained by polarization resistance measurements at 25 °C, are given in Table 4.

Table 4
Corrosion Parameters R_p, B, J_{corr}, CR & z for Copper In 0.5 M HCOOH with Addition of Imidazole Derivatives Obtained by Polarization Resistance Measurements at 25 °C

	R_p Ω-cm²	B mV	J_{corr} µA/cm²	CR mm/yr	z %
5% HCOOH	175.00	6.00	34.29	0.838	–
Inh. 1 (0.5%)	333.47	5.15	15.44	0.377	55
(1.0%)	445.33	4.81	10.79	0.264	68
(2.0%)	506.95	5.77	11.38	0.278	67
Inh. 2 (0.5%)	291.63	5.87	20.14	0.495	41
(1.0%)	437.95	4.51	10.29	0.251	67
(1.5%)	284.88	5.10	17.89	0.437	48
(2.0%)	382.37	6.32	16.54	0.404	52
Inh. 3	3710	11.13	3.00	0.073	91

Inh. 1: 4-methyl-5-hdroxymethylimidazole
Inh. 2: 1-butyl-5-methylimidazole
Inh. 3: Commercial

Discussion & Conclusions

Imidazoles are heterocyclic organic compounds with three carbon and two nitrogen atoms in the ring. The imidazole molecule shows three different anchoring sites that are suitable for surface bonding: the nitrogen atom with its lone sp2 electron pair, the C(4)H-C(5)H-"edge" and the aromatic ring.[6] The imidazoles are therefore potentially effective inhibitors. The efficiency of some imidazole derivatives as corrosion inhibitors for copper[7-10] as well as for iron[11-14] was established. In contrast to most commercial inhibitors, *imidazoles are not toxic*.

Inhibiting efficiencies of the imidazole derivatives studied were compared with the efficiency of a commercial inhibitor used in the electronics industry for copper corrosion protection in printed circuit board production.

Results obtained from the solderability and HNO_3 tests before and after the humidity chamber show that imidazole derivatives offer good inhibiting properties (Table 1). All investigated inhibitors showed good solderability before and after humidity tests. Only 1-butyl-5-methylimidazole showed poor results during HNO_3 tests conducted before humidity chamber tests.

The electrochemical investigation, performed using Tafel extrapolation, as well as polarization resistance measurements, showed small corrosion current densities for copper in all investigated solutions. The study of different inhibitor concentrations (0.5 to 2.0%) showed that 1.0 percent is optimal for the imidazole derivatives (Table 3.). The best inhibiting efficiency was shown by the commercial inhibitor at higher temperatures.

Although the imidazole derivatives showed lower inhibiting efficiency than the commercial inhibitor, imidazoles are potential corrosion inhibitors for copper. Changing of composition and structure by introduction of new active substituents can improve the inhibiting efficiency of imidazoles.

Editor's note: *Manuscript received, May 2000.*

List of Symbols Used in the Tables

B	constant (mV)
b_a, b_c	Tafel coefficients (anodic and cathodic) (mV)
CR	corrosion rate (mm/yr)
D	inhibitor layer thickness (µm)
E_{corr}	corrosion potential (mV)
j_{corr}	corrosion current density (µA/cm²)

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