Behaviour of Brasses Corrosion in Nitric Acid with and without PMT

M. Mihit,[a] **M. Belkhaouda,**[a] **L. Bazzi,**[a] **R. Salghi,**[b,*] **S. El Issami,**[a] **E. Ait Addi**[a]

[a] *Laboratoire Matériaux & Environnement, Equipe de Chimie Physique Appliquée, Faculté des Sciences, BP 8106, Agadir-Morocco.*
[b] *Laboratoire d'Ingénierie des Procédés de l'Energie et de l'Environnement, Ecole National des Sciences Appliquées d'Agadir, BP 1136, Agadir-Morocco*

Abstract

The comparative study of corrosion behaviour of brasses 70Cu30Zn and 60Cu40Zn in HNO3 solution in absence and in presence of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) was studied by gravimetric and electrochemical methods. Results obtained are in good agreement and reveal that the corrosion rate depends on immersion time and zinc content in the alloy. Copper and zinc losses from each specimen studied, at various immersion times, were estimated by Atomic Adsorption Spectroscopic analysis. This shows that the inhibition efficiency of the inhibitor towards copper is more significant than zinc. PMT was adsorbed preferentially on the copper surface and inhibits the process of corrosion of brasses in the nitric acid medium.

*Keywords:* brass, corrosion, inhibition, PMT.

Introduction

Copper is easily combined with many metals. It forms with zinc brasses which have a higher corrosion resistance and a very easy manufacture. Moreover, brasses are harder and solid. But their exhibition in acid media creates problems of corrosion [1-8]. When the brasses, containing more than 15% of zinc, are exposed in corrosive environments, they are affected not only by general corrosion damage, but also by dezincification process involving preferential dissolution of zinc, leaving a spongy mass of copper on the alloy surface [9]. Saber et al. [10] have studied the behaviour of copper-zinc alloy in nitric medium and suppose that the reactivity of HNO3 towards copper depends on the

---

autocatalytic production cycle of NO_2. Thus, copper dissolves in HNO_3 according to:

$$Cu \longrightarrow Cu^{2+} + 2e^- \tag{1}$$

$$H^+ + e^- \longrightarrow H \tag{2}$$

$$HNO_3 + H \longrightarrow H_2O + NO_2 \tag{3}$$
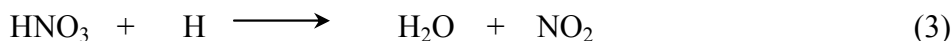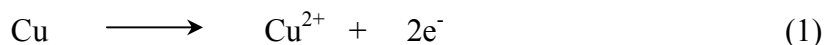
However, zinc rigorously dissociates in HNO_3 as follows:

$$Zn \longrightarrow Zn^{2+} + 2e^- \tag{4}$$

$$H^+ + e^- \longrightarrow H \tag{5}$$

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O \tag{6}$$
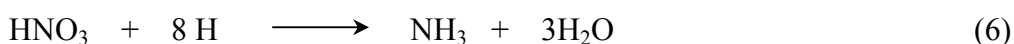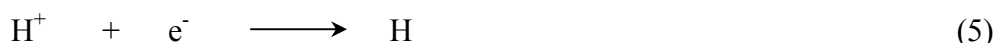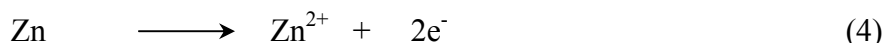
HNO_3 is more reactive to zinc than copper. The elimination of H by reactions (3) and (6) encourages the reaction (4) over the reaction (1) involving a strong dezincification [11]. Other authors noted that HNO_2 present in the solution, is very unstable and active chemically at the same time, sudden a decomposition to produce NO_3^- [12]. These anions are complexed with Cu^{2+} and Zn^{2+} according to reactions (7) and (8):

$$Cu^{2+} + NO_3^- \longleftrightarrow [Cu(NO_3)]^+ \qquad Log K= -0.01 \tag{7}$$

$$Zn^{2+} + 2NO_3^- \longleftrightarrow [Zn(NO_3)_2] \qquad Log K= -0.05 \tag{8}$$

The inhibition effect of the heterocyclic compounds is based on their chelating action and on the formation of an insoluble film on the electrode surface preventing the oxidation of the metal [13]. Thus, a barrier is easily formed by the heterocyclic molecules which contain the heteroatomes as nitrogen or sulphur [14]. The inhibitors such as imidazole [15,16], triazole [17-20] and pyrazole [21] act on the surface of copper and brasses by formation of films. Azoles are thus excellent agents of complexation on the surface of these metals.

In our laboratory, we have mainly focused on the application of tetrazole derivatives as corrosion inhibitors for copper and its alloys in different medium. The inhibition efficiency of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) was always found more important in comparison with other derivative compounds as 1,2,3,4-tetrazole (TTZ), 5-amino-1,2,3,4-tetrazole (AT) and 1-phenyl-1,2,3,4-tetrazole (PT) [22-24]. The aim of this work is to study the corrosion behaviour of the brasses 70Cu30Zn and 60Cu40Zn in nitric medium with and without the addition of PMT by using gravimetric and electrochemical measurements.

Experimental
Polarization curves were recorded with a potentiostat PGP 201, piloted by computer. The scan rate is 60 mV/min and the potential ranged from -800 to +500 mV/SCE. Before recording each curve, the working electrode is maintained with its free potential of corrosion. We used for all electrochemical tests a cell with three electrode thermostats with double wall (tacussel standard CEC/TH). Saturated calomel electrode (SCE) and platinum electrode are used as reference and auxiliary electrodes, respectively. The surface and the composition of the working electrodes are given in Table 1.

Table 1. Chemical composition (in weight percent) studied

Specimens	Cu	Zn	Fe	Sn	Al	Pb
Pure Cu	99.9	0.04	0.03	-	0.03	-
70Cu30Zn	70	28.95	0.06	0.9	0.02	0.07
60Cu40Zn	60	39.50	0.20	0.2	0.10	-
Pure Zn	-	99.90	0.30	0.3	0.20	0.20

Gravimetric tests were carried out in double distilled walled glass cell equipped with a thermostatic cooling condenser. The solution volume was 75 mL. Prior each measurement, specimens were abraded successively with fine emery papers. Then, the sheets were rinsed with acetone and distilled water, degreased and dried before being weighed and immersed in the corrosive medium. The weight-loss and the corrosion rate were determined from solution analysis by atomic absorption spectroscopy.

The corrosive solution 0.1 M HNO_3 was obtained by dilution of analytical grade 65% HNO_3 of mark Taoura with distilled water. All experiments have been performed at the temperature 25 ± 1 °C. The organic compound 1-phenyl-5-mercapto- 1,2,3,4-tetrazole (PMT) tested as inhibitor is the "Aldrich" commercial product. Its molecular structure is shown in Fig. 1.
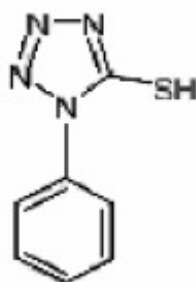

Figure 1. Molecular structure of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT).

Results and discussions
Polarization measurements
Fig. 2 and Fig. 3 represent, respectively, the polarization plots of 70Cu30Zn and 60Cu40Zn in 0.1 M HNO$_3$ with and without PMT at 10^{-3}M after 24 hours of immersion. Cathodic current-potential curves give rise to Tafel lines indicating that the hydrogen evolution is activation-controlled.
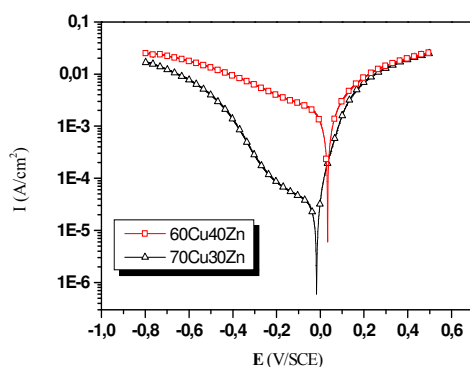

Figure 2. Polarization plots of brasses studied in 0.1 M HNO$_3$ after 24 h of immersion.
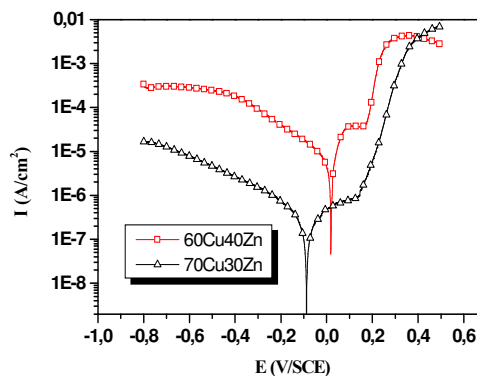
Figure 3. Polarization plots of brasses studied in 0.1 M HNO$_3$ + 10^{-3} M PMT after 24 h of immersion.

Electrochemical parameters derived from Fig. 2 and Fig. 3 are gathered in Table 2. The corrosion inhibition efficiency E$_I$(%) was defined as:

$$E_I(\%) = (1 - \frac{I'_{corr}}{I_{corr}}) \times 100$$

where I_{corr} and I'_{corr} are, respectively, the uninhibited and inhibited corrosion current densities determined by extrapolation of the cathodic Tafel lines to corrosion potential (E_{corr}).

Table 2 indicates that the corrosion rates of 60Cu40Zn alloy are greater than those of 70Cu30Zn in the corrosive medium with and without the addition of the inhibitor. These results demonstrate that 60Cu40Zn is less resisting against the effect of nitric medium. On the other hand, we noted that PMT inhibited the corrosion of tow brasses with a value exceeding 99%.

Table 2. Corrosion data of the tow brasses studied in 0.1 M HNO$_3$ with and without addition of 10^{-3} M PMT.

alloys	solution	E$_{corr}$ (V/SCE)	I$_{corr}$ (μA/cm^2)	βc (mV/dec.)	E$_I$ (%)
70Cu30Zn	Blank (S)	-0.018	44	-133	-
	(S) + PMT	-0.088	0.4	-135	99.1
60Cu40Zn	Blank (s)	0.032	2130	-145	-
	(S) + PMT	0.018	9	-133	99.6

Weight loss measurement
The evolution of the corrosion rate of brasses 70Cu30Zn and 60Cu40Zn with immersion time, in nitric acid with and without PMT at 10^{-3} M, is shown in Fig. 4 and Fig. 5. It's clear, in both cases, that the corrosion rate of 60Cu40Zn is always more important than that of 70Cu30Zn. This difference in resistance is due to the zinc content in the alloy. Other studies found that the corrosion rate depends on the zinc content in the alloy [9,26].
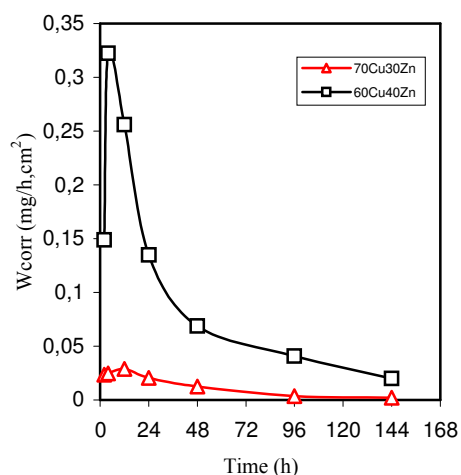

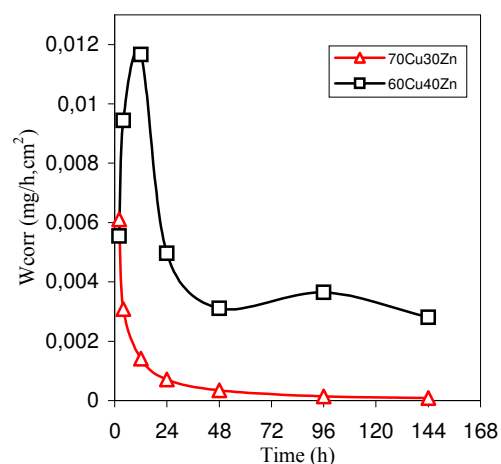**Figure 4**. Variation of corrosion rate of brasses (Cu and Zn dissolution) with immersion time in 0.1 M HNO_3.

Figure 5. Variation of corrosion rate of brasses (Cu and Zn dissolution) with immersion time in 0.1 M HNO_3 + 10^{-3} M PMT.

Figs. 4 and 5 indicate that the evolution of corrosion rate with the immersion time presents the maximum Wmax at a critical time Tc. Table 3 gives the value of these times Tc in the case of both 70Cu30Zn and 60Cu40Zn. The addition of PMT causes change on the value of the critical time Tc. This period increases from 5 to 10 hours in the case of 60Cu40Zn and it decreases from 12 to 2 hours in the case of 70Cu30Zn. For times superior at Tc, the corrosion rate decreases; this decrease is probably due to the formation of a deposit of the corrosion product on the metallic surface. In order to have an adequate explanation, we made quantitive analysis of copper and zinc components in the solution by atomic absorption spectroscopy.

Table 3. Critical time Tc related to 70Cu30Zn and 60Cu40Zn in 0.1 M HNO_3 with and without 10^{-3} M PMT.

	Critical time T_C (h)	
	Blank	Blank + PMT
70Cu30Zn	12	< 2
60Cu40Zn	5	10

Figs. 6 and 7 show the evolution of corrosion rate of the components (dissolved Cu and Zn) of both 70Cu30Zn and 60Cu40Zn as a function of the exposure time

in nitric acid in absence and presence of PMT, respectively. In the blank solution (Fig. 6), the corrosion rate of copper is important compared with zinc from the first minutes of immersion in the case of 70Cu30Zn, whereas the corrosion rate of copper is also important, but only after 3 hours of immersion time of 60Cu40Zn. These results explain that the zinc corrodes more selectively than copper [4,9,27]. The addition of PMT at 10^{-3} M slows down the dissolution rate of both components (Cu and Zn); however, we noted that the corrosion rate of zinc, in this case, is more important than that of copper. It is suggested in this subject that PMT has a selective protection of the site in which copper exists.
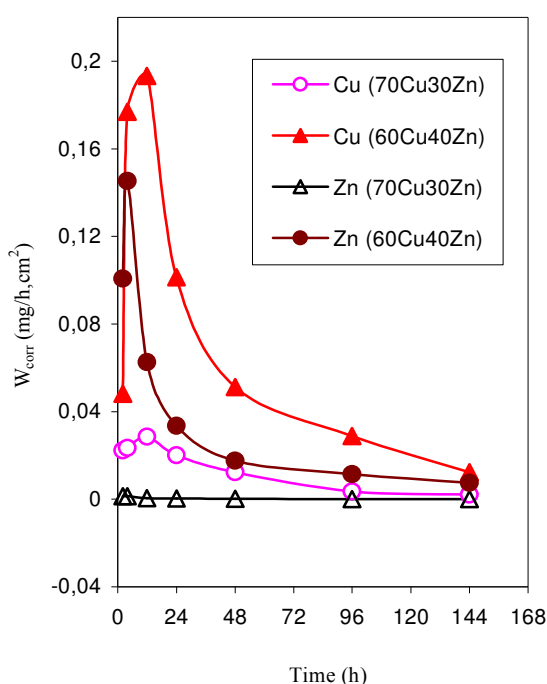

Figure 6. Variation of Cu and Zn dissolution from 70Cu30Zn and 6OCu40Zn brasses with immersion time in 0.1 M HNO$_3$.
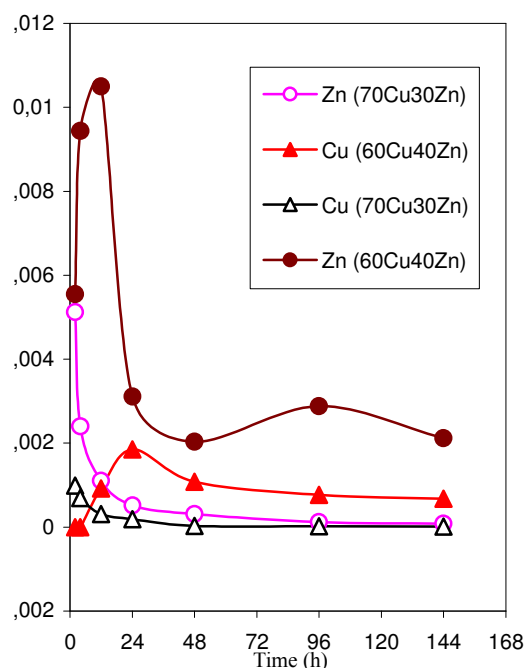

Figure 7. Variation of Cu and Zn dissolution from 70Cu30Zn and 6OCu40Zn brasses with immersion time in 0.1 M HNO$_3$ + 10^{-3}M PMT.

The values of critical immersion time Tc, relating to the maximum of the corrosion rate of copper and zinc components relating to each specimens, are gathered in table 4. It is noted that Tc values, related to 60Cu40Zn components, increase in the presence of PMT. However, Tc values decrease in the case of the constituents of 70Cu30Zn. In this connection, it is suggested that the alloy requires minimum and enough time to the dissolution of superficial zinc, then the PMT adsorbs on the alloy surface which is rich of copper; therefore, the alloy containing 40% of zinc needs more time than that containing 30%. This is the reason why the PMT inhibitor prevents quickly the dissolution of 70Cu30Zn components.

Table 4. Critical time Tc values relating to the dissolution of Cu and Zn constituents in the case of 70Cu30Zn and 60Cu40Zn in 0.1 M HNO$_3$ with and without PMT at 10^{-3} M.

		Critical time Tc (h)	
		Blank	Blank + PMT
70Cu30Zn	Cu	12	<2
	Zn	<2	<2
60Cu40Zn	Cu	10	24
	Zn	5	10

Fig. 8 illustrates the evolution of the inhibition efficiency (E$_w$%) of PMT towards the dissolution of Cu and Zn from 70Cu30Zn and 60Cu40Zn as a function of the immersion time. The value of (E$_w$%) is calculated as follows:

$$E_w(\%) = (1 - \frac{W'_{corr}}{W_{corr}}) \times 100$$

where W$_{corr}$ and W'$_{corr}$ are, respectively, the uninhibited and inhibited corrosion rate of the component (Cu or Zn).

Fig. 8 shows the evolution of the inhibition efficiency of PMT, with immersion time, towards components of each alloy studied. We concluded that the PMT protection towards copper component is more significant in comparison with zinc. Consequently, the inhibition efficiency related to zinc decreases while the zinc content increases in the alloy.
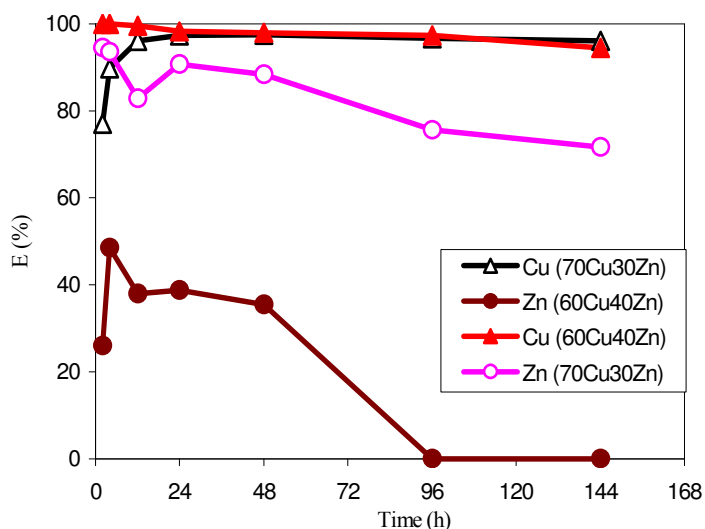
Figure 8. Evolution of the inhibition efficiency of PMT of alloys' components with the immersion time.

Gravimetric survey of the behaviour of pure copper and zinc
According to the experimental methods used, we investigated the corrosion and the corrosion inhibition of pure copper and zinc using PMT at 10^{-3}M under the same experimental conditions. Fig. 9 and Fig. 10 illustrate, respectively, the

evolution of the corrosion rate of both pure metals studied as a function of immersion time. The addition of PMT slows down the kinetic of copper dissolution. However, the behaviour of the zinc doesn't change. We noted that PMT is not adsorbed on the zinc surface. The immersion time Tc relating to the maximum corrosion rate is unchanged either for pure copper or zinc. These results explain that the variation of Tc related to the studied brasses is due essentially to simultaneous existence of copper and zinc in the alloys.

These observations are consistent with other author's results [13,27,28]. They found that there is the formation of Cu-PMT complex on the surface, especially with the heteroatom of PMT (N and S) [13,29]. This result suggests that the PMT coordination compound film stabilizes Cu^+ and blocks the substrate electrochemical reaction, thus preventing the metal from corrosion.
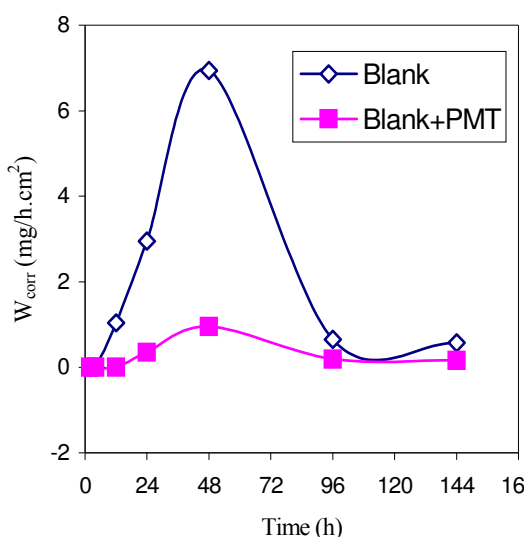
Figure 9. Evolution of corrosion rate of pure copper with the immersion time in 0.1 M HNO_3 with and without the addition of 10^{-3} M of PMT.
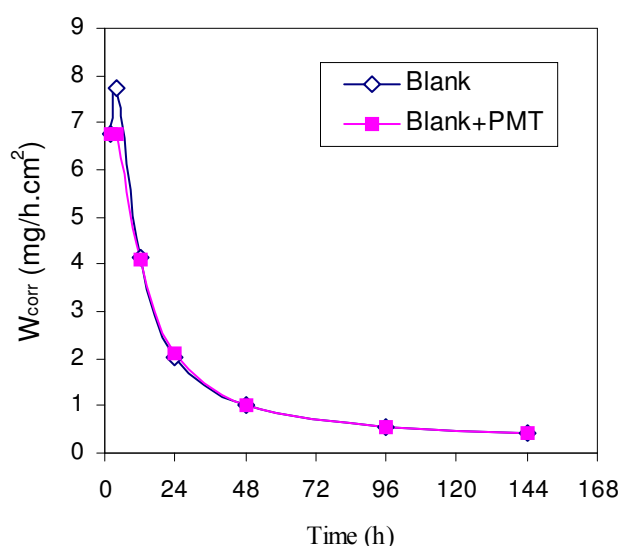
Figure 10. Evolution of corrosion rate of pure zinc with the immersion time in 0.1 M HNO_3 with and without the addition of 10^{-3} M of PMT.

Conclusion

The main findings of the present work can be summarized as follows:

1. 0.1 M HNO_3 is a corrosive medium to 70Cu30Zn and 60Cu40Zn alloys.
2. The corrosion rate depends on the immersion time and on the zinc content in the alloy.
3. The addition of PMT slows down the oxidation of brasses.
4. The PMT adsorbs and protects copper, however it remains with no effect on the zinc.

References

1. S. Kertit, H. Essoufi, B. Hammouti and M. Benkaddour,. *Chim. Phys*. 95 (1998) 2070.
2. R. Karpagavalli, S. Rajeswari, *Anti-corr. Meth. and Mat*. 45 (1998) 333.
3. W.A. Badawy, F.M. Al-kharafi, *Corrosion Science* 55 (1999) 268.
4. M.I. Abbas, *Br. Corr. J.* 26 (1991) 273.
5. S. Kertit, B. Hammouti, *Applied Surf. Sci*. 93 (1996) 59.
6. S.S. El-Egamy, A.S. El-Azeb, W.A. Badawy, *Corrosion Science* 50 (1994) 468.
7. S. El Issami, L. Bazzi, M. Mihit, M. Hilali, R. Salghi, E. Ait Addi, *Physique IV* 123 (2003) 307.
8. Y. Abed, Z. Anaz, B. Hammouti, A. Aouinti, S. Kertit, A. Mansri, *J. Chim. Phys*. 96 (1999) 96.
9. S.N. Banerjee, "An introduction to science of corrosion and its inhibition" Oxanian Press, New Delhi, (1985) P 286; P.T. Gilbert in "Corrosion" (Eds.) L.L. Shreir, Newness-Butterworths, London (1979) 4:46
10. T.M.H. Saber, A.A. El Warraky, *Brit. Corr. J.* 26 (1991) 279.
11. A.M. Shams El Din, A.E. El Hosary, M.M. Gawish, *Corrosion Science* 16 (1976) 845.
12. B. Malki, Thèse de doctorant es sciences, sciences des matériaux, Lille, (1999).
13. X.R. Ye, X.Q. Xin, J.J. Zhu, Z.L. Xue, *Applied Surf. Sci*. 135 (1998) 307.
14. I. Popova, J.T. Yates, *J. Langmuir* 13 (1997) 6169.
15. E. Stupnisek-Lisac, A. Gazivoda, M. Madzarac, *Electrochimica Acta* 47 (2002) 4189.
16. G. Lewis, *Corrosion Science* 22 (1982) 579.
17. A.M. Fenelon, C.B. Breslin, *J. Applied Electrochem*. 8 (2001) 509.
18. H.S. Hegazy, E.A. Ashour, B.G. Ateya, *Applied Electrochem*. 5 (2001)1265.
19. R. Ravichandran, S. Nanjundan, N. Rajendran, *Applied Surf. Sci*. 236 (2004) 241.
20. G.K. Gomma, *Material Chemistry and Physics* 56 (1998)27.
21. A. Dafali, B. Hammouti, R. Touzani, S. Kertit, A. Ramdani, K. El Kacemi, *Anti-Corrosion Methods and Materials* 49 (2002) 96.
22. M. Mihit, S. El Issami, M. Bouklah, L. Bazzi, B. Hammouti, E. Ait Addi, R. Salghi, S. Kertit, *Applied Surf. Sci.* 252 (2005) 2389.
23. S. El Issami, L. Bazzi, M. Mihit, M. Hilali, R. Salghi, E. Ait Addi, *J. Phys. IV France* 123 (2005) 307.
24. M. Mihit, R. Salghi, S. El Issami, L. Bazzi, B. Hammouti, E. Ait Addi, S. Kertit, *Pigment and Resin Technoloy* 35 (2006)151.
25. S. El Issami, M. Mihit, L. Bazzi, R. Salghi, M. Hilali, E. Ait Addi, *Transaction of SAEST* 40 (2005) 24.

26. J. Sugawra, H. Ebike, *Corrosion Science* 7 (1967) 513.

27. R. Karpagavalli, S. Rajeswari, *Bulletin of Electrochemistry* 15 (1999) 56.

28. E.S. Raper, *Coord. Chem. Rev*. 61 (1985) 115.

29. J.L. Fang, X.R. Ye, J. Fang, Y.L. Chen, *J. Nanjin Univ*. 28 (1992) 569.