Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(5):173-177
(http://derpharmachemica.com/archive.html)

Corrosion performance by epoxy zinc -rich coating containing 4,4′-ethylene bis (N, N diglycidylaniline) on copper substrate.

O. Dagdag[1*], M. Rafik[1], S. E. Hegazi[1], A. Essamri[1], M. Ebn Touhami[2], M. El Gouri[1,3], M. Assouag[4] and A. El Harfi[1]

[1]*Laboratoire d'Agroressources, Polymères et Génie des Procédés - Equipe de Chimie Organique et Polymères, Département de Chimie, Faculté des Sciences, Université Ibn Tofail, BP 133, 14000 Kenitra, Maroc*
[2]*Laboratoire d'Ingénierie des Matériaux et d'Environnement : Modélisation et Application (LIMEMA), Equipe de Corrosion Application et Modélisation, Département de Chimie, Faculté des Sciences, Université Ibn Tofail, BP 133, 14000 Kenitra, Maroc*
[3]*Laboratoire de Génie des Procédés, d'Energies Renouvelables et d'Environnement, Département de Génie des Procédés, Ecole supérieure de technologie, Université Sidi Mohammed Ben Abdallah, Fès, Maroc*
[4]*Equipe Matériaux Avancés et Applications ENSAM, Université Moulay Ismail, B.P. 15290 Al Mansour, Meknès, Morocco*

ABSTRACT

In this work, we studied the impact of copper coatings by epoxy resin 4, 4′- Ethylene bis (N, N diglycidylaniline) whose thickness of the deposited film on the substrate is estimated at 170 ± 10 µm. To evaluate this impact of coating, we used the electrochemical impedance spectroscopy (EIS) and scanning electronic microscopy (SEM) were used in this study. The experimental results obtained by the EIS method of copper gave the polarization resistance (R_p) equal to 15240 Ω.cm². This shows that the effect of the coating of copper investigated by the resin is more effective in 3 % NaCl compared to the uncoated one in 3 % NaCl. Subsequently, we have studied the impact of coated copper with a formulation of conducted a new formulation by adding of inorganic filler in the matrix of protection 4, 4′- Ethylene bis (N, N diglycidylaniline) in the presence of 5% of zinc leads us to an experimental value R_p = 44240 Ω.cm². The effectiveness is equal to 97% in 3 % NaCl.

Keywords: copper, epoxy resin, coating, electrochemical impedance spectroscopy, scanning electronic microscopy and 3 % NaCl.

INTRODUCTION

Copper and its alloys are very widely used materials for their excellent electrical and thermal conductivities in many applications such as electronics and integrated circuits. Copper is resistant toward the influence of atmosphere and many chemicals. However, it is susceptible to corrosion in aggressive media, such as Cl^- [1–14].

Organic coatings are the most widely used method of metal bodies protection from atmospheric corrosion. The paint film acts as a physical barrier between corrosive electrolyte and copper substrate. However, it is well known that the coating is permeable to water, oxygen and corrosive ions which are presented in the corrosive electrolyte. Moreover, using organic coatings, the spread of corrosive products will be prevented at the initial sites of electrolyte permeation into the metal surface. Therefore, the adhesion forces which attach the coating to the metal surface can also affect the coating corrosion performance [15–19].

Different parameters including the number of pores, ionic resistance of coating against electrolyte diffusion and the cross-linking density of the coating can affect the coating resistance against electrolyte diffusion through coating matrix.

Epoxy is one of the most common barrier coating material used in severe corrosion environments including marine environment [20,21]. Due to the hydrophilic chemical groups of cured epoxy structure (such as hydroxyl group (–OH), carboxyl group (C=O), phosphine oxide group (P=O) and amino group (N–H)), epoxy has exhibited hydrophilic properties. This property of epoxy coating causes a negative effect on its protectiveness ability of underneath metal. So therefore, there has been a lot of effort to improve the protectiveness of epoxy coatings, considering their coating thickness and surface treatment methods.

MATERIALS AND METHODS

Tetrafunctional epoxy resins

Tetrafunctional epoxy resin was synthesized by reacting 4,4′- Ethylene bis (N, N diglycidylaniline) with epichlorohydrin.

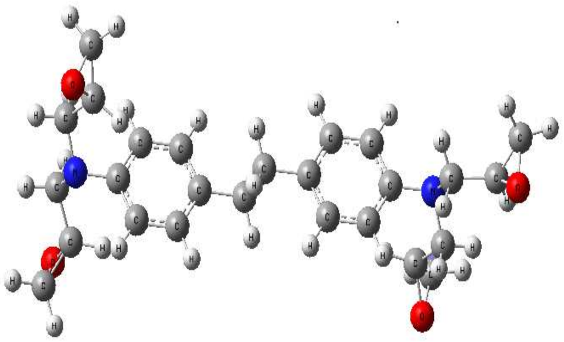

Figure 1. Shows the chemical structure of 4, 4′- Ethylene bis (N, N diglycidylaniline)

Amine type curing agents are one of the basic curing agents for epoxy resins, and they can be classified into three major categories: aliphatic, aromatic, or cycloaliphatic amines.

Amine type curing agents are one of the basic curing agents for epoxy resins, and they can be classified into three major categories: aliphatic, aromatic, or cycloaliphatic amines. Amine type curing agents react with epoxide rings by nucleophilic addition. We limited ourselves to one hardener class: aromatic amine. According to their chemical structure. Figure 2 shows the chemical structure of 4, 4-diaminodiphenyl methane (DDM).

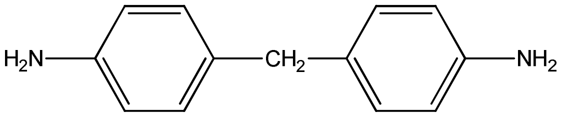

Figure 2. Chemical structure of DDM

Evaluation of corrosion-resistant properties of the coating

The corrosion protection properties of the coatings were tested using electrochemical impedance spectroscopy (EIS) measurements, which were performed on Voltalab PGZ100 potentiostat in a conventional three-electrode cell. The coated carbon steel was used as the working electrode, a large platinum plate was used as the counter electrode, and the Ag/AgCl (saturated KCl) electrode was used as the reference electrode. The test solution was a 3 % sodium chloride solution. All tests were conducted at room temperature (25 °C) and open to air.

EIS measurements were performed over a frequency range of 100 kHz to 0.1 Hz by using a 10 mV amplitude sinusoidal voltage at open cycle potential (OCP). The data were acquired in four cycles at each frequency to obtain good precision at all frequencies. All experiments are performed at the open circuit potential. The obtained impedance data are analyzed in terms of equivalent electrical circuit using Bouckamp’s program.

The morphology of the coatings was characterized using scanning electron microscopy (SEM, JEOL-JSM 5500). The analysis is performed with an acceleration voltage of 0.5-30 kV.

RESULTS AND DISCUSSION

Electrochemical measurements by electrochemical impedance spectroscopy

The results of this method are shown as Nyquist plots. These copper impedance diagrams which are immersed for 40 minutes before each measurement in an open circuit in the corrosive solution 3% NaCl vis-a-vis all matrices are grouped in Figure 3.

The analysis of the different diagrams corresponding respectively to the protective matrices shows that the latter are formed by two capacitive loops : one with high frequency (HF) assigned to the film effect and the other with low frequency (LF) which is generally attributed to the charge transfer process. This is due to the phenomenon diffusion. Indeed, the larger the diameter of a semicircle longer increases, the better will be the corrosion resistance of the protective film.

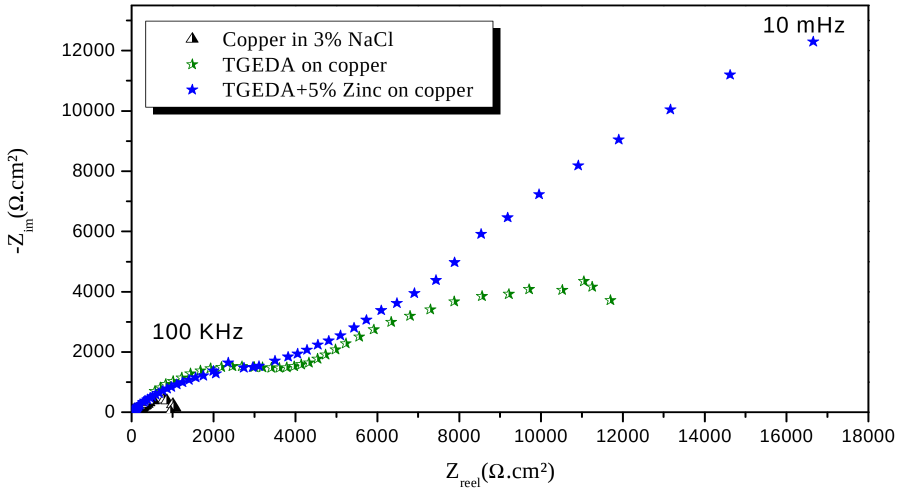

Figure 3. Electrochemical impedance diagrams with open circuit after 40 min of immersion for copper in 3% NaCl in the presence of matrices MP_1 and MP_2 at 298 K

The values of électrochemical impedance and the protective efficiency résulting from each matrice of protection MP_1 and MP_2 are summarized in Table 1.

This table shows that the values of the polarization resistance (R_p) for the four coating matrices are evaluated between 15.10^4 and 44.10^4 Ω.cm².

On this basis, the largest semi-circle in the Nyquist diagram of MP_2 coating system indicates a better corrosion resistance, which can be explained by the presence of the Zinc responsible for higher corrosion resistance.

Table 1 summarizes the various electrochemical parameters obtained from the impedance diagrams

Protective matrices (MP)	R_s (Ω.cm²)	C_f (µF/cm²)	R_{pf} (Ω.cm²)	C_{dl} (µF/m²)	R_{ct} (Ω.cm²)	R_p (Ω.cm²)	*E* %
Copper	20	-	-	-	950	1200	-
MP_1	540	41.5	1950	18.62	13830	15240	92%
MP_2	638	30.09	2700	5.02	44160	46222	97%

Observations of Surface condition by SEM.

To confirm the results obtained by the électrochemical measures for the two matrices with standard coating (MP_1) and loaded (MP_2) by zinc (Zn), we used as a means of analysis the coating surface on copper in 3% NaCl after the immersion for 48 hours at 298 K.

Figure 4 shows the SEM morphologies of the state of copper surface immersed in 3% NaCl for 48 h at 298 K for two sample.

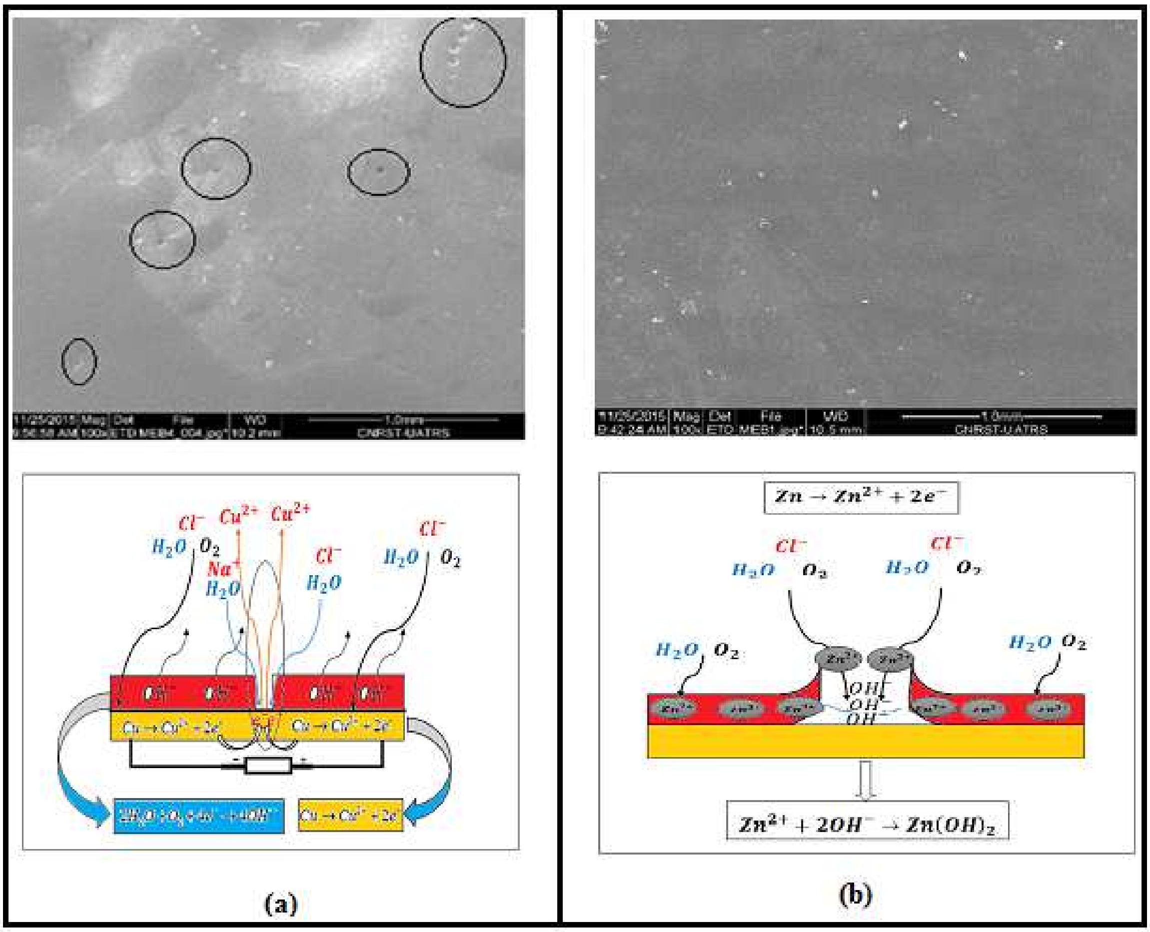

Figure 4. SEM images for the four samples after the immersion for 48 hours in 3% NaCl

a) Coating matrix by the MP_1

The standard protective matrix MP_1 submerged during the same interval of time in a 3% NaCl solution. As shown in figure 4 (a), we expect that there is a relatively large spread of electrolytes (chloride ions) through the protective film which may present micropores / defects while inducing a primary corrosion.

b) Coating by the matrix MP_2

In addition, the SEM micrography during the application of the matrix MP_2, we observed in the film surface of the coating some white spots considered as corrosion products according to the literature and this shows that it is concerned with the zinc oxide layer which is necessary for the protection of passivation of metals issued from the couple Zn / Zn^{2+} according to equations (4 b).

This can be explained by a synergistic effect provided by the coating of passivation issued (Zn / Zn^{2+}).

CONCLUSION

In this study we carried out the protection of the copper by the coating method issued from the formulations which are based on a standard oxide polymer (MP_1) and a zinc inorganic filler (MP_2). This was done in order to decrease the corrosive effect of the medium on the substrate (usually copper).

The main findings of this study can be drawn as follow:

1. The corrosion protective effect of the formulated matrix MP_2 gave us the best results.
2. The SEM observation shows that the surface of the matrix based on a polymer loaded with zinc deposited on carbon steel completely protected is due to the formation of a protective layer which limits the penetration of electrolyte through the protective film.

REFERENCES

[1] D Tromans; R Sun. *J. Electrochem. Soc.*,**1991**, 138: 3235–3244.

[2] L Núnez; E Reguera; F Corvo; E Gonzalez; C Vazquez. *Corros. Sci.*, **2005**, 47: 461–484.
[3] A El Warraky; H.A El Shayeb; E.M Sherif. *Methods Mater.*, **2004**, 51: 52–61.
[4] A L Bacarella; J C Griess. *J. Electrochem. Soc.*, **1973**, 120: 459–465.
[5] H P Lee; K Nobe. *J. Electrochem. Soc.*, **1986**, 133: 2035–2043.
[6] T Hoepner; S Lattemann. *Desalination.*, **2002**, 152: 133–140.
[7] J G Hamilton; J C Farmer; R J Anderson. *J. Electrochem. Soc.*, **1986**, 133: 739–745.
[8] C B Breslin; D D Macdonald. *Electrochim. Acta.*, **1998**, 44: 643–651.
[9] E Rocca; G Bertrand; C Rapin; J C Labrune *J. Electrochem. Soc.*, **2001**, 503: 133–140.
[10] V Lakshminarayanan; K Kannan; S R Rajagopalan. *J. Elec-trochem. Soc.*, **1994**, 364: 79–86.
[11] R K Dinnappa; S M Magannas. *Corsos. Sci.*, **1987**, 27: 349–361.
[12] J D Talati; D K Gandhi. *Corros. Sci.*, **1983**, 23:1315–1332.
[13] M Fleischmann; I R Hill; G Mengoli; M M Musiani; J Akhavan. *Electrochim. Acta.*, **1985**, 30 :879–888.
[14] M Fleischmann; G Mengoli; M M Musiani; C Pagura. *Electrochim. Acta.*, **1985**, 30: 1591–1602.
[15] G Bierwagen; D Tallman; J Li; L He; C Jeffcoate. *Prog. Org. Coat.*, **2003;** 46: 148–157.
[16] C G Oliveira; M G S Ferreira. *Corros. Sci.*, **2003**, 45: 123–138.
[17] J Havlik; A Kalendova; D Vesely. *J. Phys. Chem. Solids.*, **2007**, 68 (5): 1101–1105.
[18] H L Yang; F C Lin; E H Han. *Prog. Org. Coat.*, **2005**, 53: 91–98.
[19] Y Gonzalez-Garcia; S Gonzalez; R M Souto. *Corros. Sci.*, **2007**, 49: 3514–3526.
[20] C A May; Epoxy Resins : Chemistry and Technology, Marcel Dekker, New York, **1988**.
[21] T M Goulding; A Pizzi; K L Mittal, Handbook of Adhesive Technology, Marcel Dekker, New York, **1994**.