Int. J. Electrochem. Sci., 13 **(2018)** 8944 – 8952, doi: 10.20964/2018.09.42

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Short Communication

Effect of Curing Agents on the Photodegradation of Epoxy Coatings investigated by Electrochemical Impedance Spectroscopy

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Received: 2 May 2018 / *Accepted:* 28 June 2018 / *Published:* 5 August 2018

The photo-degradation behavior of LMPAR/DGEBA epoxy coatings under UV irradiation and the influence of the curing-agent molar ratio on water resistance were investigated using electrochemical impedance spectroscopy. After exposure to UV irradiation for 88 hours, a post-curing process as well as the formation of carbonyl groups increased the low frequency impedance, in comparison to the as-prepared sample. By increasing the irradiation time from 208 hours to 399 hours, the modulus values decreased, probably due to the generation of some micro-defects near the sample surfaces. After 543 h of irradiation, the lower modulus values and the emergence of a second time constant implied that an interfacial corrosion reaction occurred. Considering the anti-photodegradation of the epoxy coating, the optimal LMPAR/ DGEBA molar ratio was approximately 0.415, at which the water uptake and the porosity of the epoxy coating were relatively low, and the EIS spectra showed the characteristics of a highly cross-linked structure in the coatings.

Keywords: Epoxy coating, photodegradation, water resistance, electrochemical impedance spectroscopy

1. INTRODUCTION

Diglycidyl ether of bisphenol-A (DGEBA) epoxy resins have been extensively used in industry, such as protective coatings, material adhesions, and electronic engineering. [1]. However, epoxy resin is prone to degradation under various environmental conditions such as humidity, heat or light, which profoundly limit their applications [2-5]. Among these conditions, photodegradation is one of the most principal ageing processes. It was found that the photo-initiating species are essentially derived from the phenoxy part, whereas the evolution of chemo-physical microstructures of the epoxy resins

principally relies on both the amine concentration and the electron density of nitrogen atoms in benzene rings [6-10]. Meanwhile, the moiety of the curing agent also affects the photooxidation process [11] and the water resistance [12,13]. However, few studies have focused on the influence of the curing agent ratio on water resistance of epoxy coatings during the photoaging process.

Electrochemical impedance spectroscopy (EIS) is one of the powerful techniques to examine the water permeation of the insulator coatings [14,15]. The impedance spectroscopy is sensitive to the porous structure of the polymers [16, 17]. In this work, epoxy coatings with different LMPAR/DGEBA molar ratios were prepared, and the effect of the curing agent dosage on the water resistance and the anticorrosion performance of the coatings during the photoaging process were studied systematically using electrochemical impedance spectroscopy.

2. EXPERIMENTAL

2.1 Materials

The diglycidyl ether of bisphenol-A (DGEBA) epoxy resin E51 was purchased from Jiangsu San Group Corporation, China, and the low molecular polyamide resin (LMPAR) 651 was provided by Yueyang Zhongzhan Science & Technology Co., Ltd. The epoxy value of E51 was 0.51 mol/100g. The mixture of DGEBA and LMPAR was coated on a carbon steel substrate, and was subsequently cured at 80 ^{o}C for 3 hours. The mixing molar ratios (LMPAR to DGEBA) were 0.221, 0.318, 0.415, 0.515 and 0.613. The film thickness of dry epoxy was approximately 30 μm.

2.2 Ultraviolet Ageing

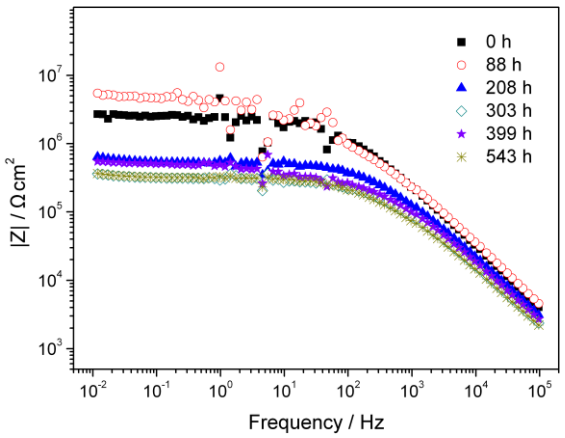
The ultraviolet ageing process was conducted using commercial UV-A lamps (340 nm for the center wavelength of UV light). The treatment temperature was maintained at 60 ^{o}C. The film samples were irradiated by UV light for different times: 0, 88, 303, 399, and 543 hours.

2.3 EIS measurement

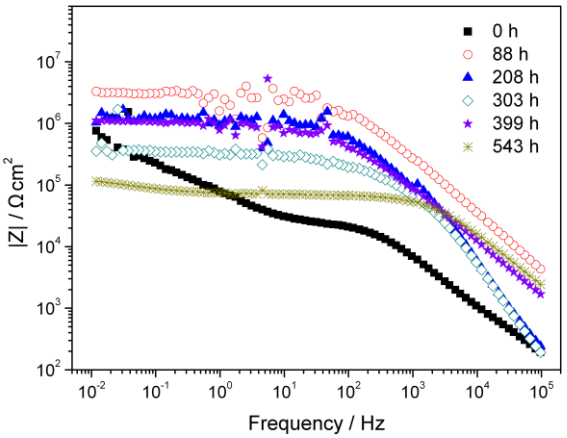
EIS measurements were performed with a classic three-electrode cell on an electrochemical workstation (Corrtest CS310) in a 3.5 wt% NaCl aqueous solution. The epoxy-coated steel was used as the working electrode with an area of 1.0 cm^2. A saturated calomel electrode and a platinum electrode were applied as the reference electrode and the counter electrode, respectively. Impedance spectra were taken every 0.17 hours in the frequency ranging from 100 kHz to 0.1 Hz during the first 1.67 hours of immersion, and then in a range of 100 kHz to 0.01 Hz. The detailed experimental parameters are the same as those in the previous reference [18].

3. RESULTS AND DISCUSSION

Figure 1 shows the impedance spectra of the epoxy coatings (a LMPAR/ DGEBA molar ratio of is 0.415) that were UV-treated for different amounts of time after being immersed in a NaCl solution for 24 hours or 168 hours. The impedance modulus in the low-frequency region at the early stage (88 hours) was obviously higher than that of the sample without UV-treatment, indicating that a post-curing process exists at the initial stage of UV-irradiation. Similar results of the post-curing of epoxy induced by UV treatment were also reported by previous studies [18,19]. It was also found that the impedance modulus at low frequencies decreased with increasing time of ageing. The value of the modulus at 0.01 Hz decreased from 5.5×10^6 Ω cm^2 (for 88 hours UV-aging) to 6.4×10^5 Ω cm^2 (for 208 hours) and 3.6×10^5 Ω cm^2 (for 303 hours) or from 3.3×10^6 Ω cm^2 (for 88 hours) to 1.0×10^6 Ω cm^2 (for 208 hours) and 3.5×10^5 Ω cm^2 (for 303 hours) for the samples immersed in a 3.5% NaCl solution for 24 hours and 168 hours, respectively.



(a)



(b)

Figure 1. Impedance diagrams (Bode plots) of the LMPAR/DGEBA epoxy coating with a molar ratio of 0.415 irradiated by UV light for 0 hours, 88 hours, 208 hours, 303 hours, 399 hours and 543 hours. The test sample was immersed in a 3.5% NaCl solution for 24 hours (a) and 168 hours (b).

It is likely that some micro-defects formed near the surface of the film sample after UV-treatment for 208 hours because of molecular chain scission, which resulted in a drastic decrease in the barrier property. The EIS results are in agreement with the results probed by positrons [20].

For the sample UV-treated for 303h, the low-frequency impedance value after 24 h (Figure-1a) of immersion was much higher than that of the sample treated for 303 hours, while the impedance curve of the sample irradiated for 543 hours coincided with that of the one irradiated for 303 hours. After immersion for 168 hours (Figue-1b), the impedance modulus in the low frequency region was still higher than that of the sample irradiated for 303 hours. However, for the sample irradiated for 543 hours, the low frequency impedance decreased significantly. This value was much lower than that of the sample irradiated for 303 hours and that of the second time constant relevant to the interfacial reaction in the coatings appeared. Zheng's work suggested that free radicals may form in a polymer due to UV irradiation and that these free radicals may induce the formation of a dense layer on the surface [21]. Thus, the results shown above in Figure 1 may be contributed to the formation of a dense layer on the sample surface. The free radicals generated upon UV-irradiation for 303 hours might have recombined and formed novel dense structures, which effectively encloses some relatively small defects in a much deeper sub-layer. As the irradiation time increased to 543 hours, a long-term protection for the steel substrate could not be achieved using the epoxy coating.

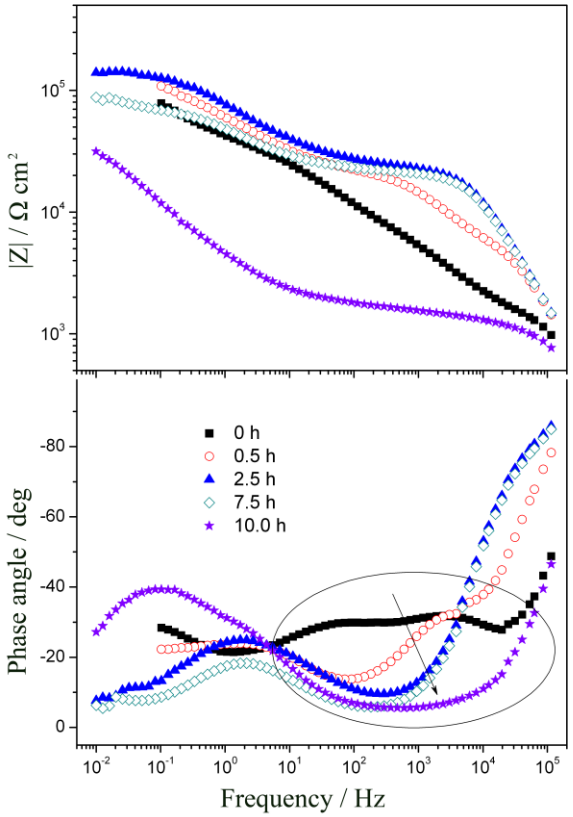


Figure 2. Impedance diagrams (Bode plots) of the epoxy coatings (a LMPAR/DGEBA ratio of 0.318) irradiated by UV light for 543 hours after different immersion times (0 hours, 0.5 hours, 2.5 hours, 7.5 hours and 10 hours) in a 3.5% NaCl solution.

According to the discussion above, the electrochemical performances of the epoxy coatings treated by UV-irradiation for 543 hours were investigated to understand the effect of the curing agent dosage on the water resistance and the anticorrosion properties. Figure 2 presents the impedance spectra for the UV-treated epoxy coatings with a LMPAR/ DGEBA molar ratio of 0.318 after being immersed in a 3.5% NaCl solution for different amounts of time. It can be observed from the phase angle that an overlap in the time constants occurs at high frequencies (50 ~ 3000 Hz) at the initial stage of immersion. This phenomenon is ascribed to the increasing density and cross-sectional area of the surface micropores. However, the water resistance performance related to micropores is not observed. Addtionally, the time constant at high frequencies associated with microporous structures also disappeared completely after 2.5 hours of immersion, which means the coating surface lost its blocking effect on the electrolyte solution. At low frequencies, the Bode modulus was approximately 1.0×10^5 Ω cm^2 at the initial stage of immersion; then, it decreased to 3.0×10^4 Ω cm^2 after 10h of immersion.

Figure 3 shows the impedance spectra of the epoxy coatings with a LMPAR/DGEBA molar ratio of 0.613 after being exposed to UV light for 543 hours. It is demonstrated that only the impedance modulus in the low-frequency region changed during in 10 hours of immersion, which means the corrosion behavior occurs at the interface between the coating and the substrate. The impedance characteristics associated with a microporous structure and a high-density structure were not observed. The Bode modulus in the low frequency region stayed close to 10^4 Ω cm^2, indicating that the water resistance of the coating was weakened due to UV irradiation for longer than 543 hours.

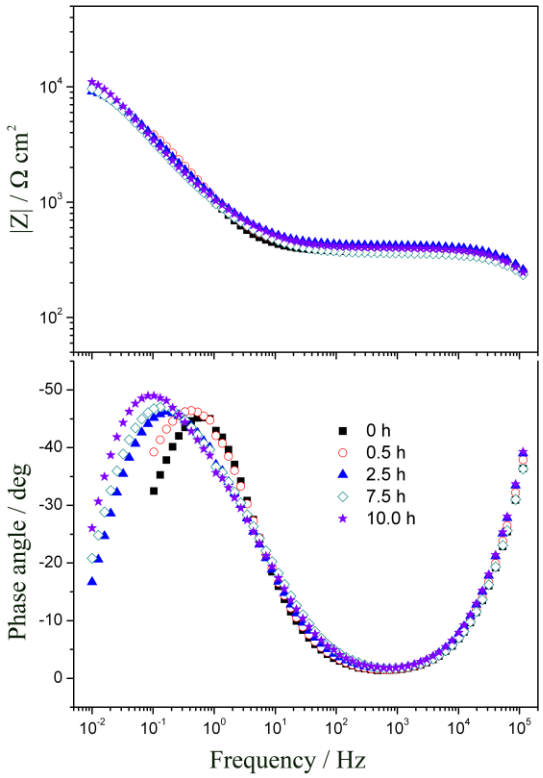


Figure 3. Impedance diagrams (Bode plots) of the epoxy coatings (a LMPAR/DGEBA ratio of 0.613) treated with UV-irradiation for 543 hours after different immersion times in a 3.5% NaCl solution.

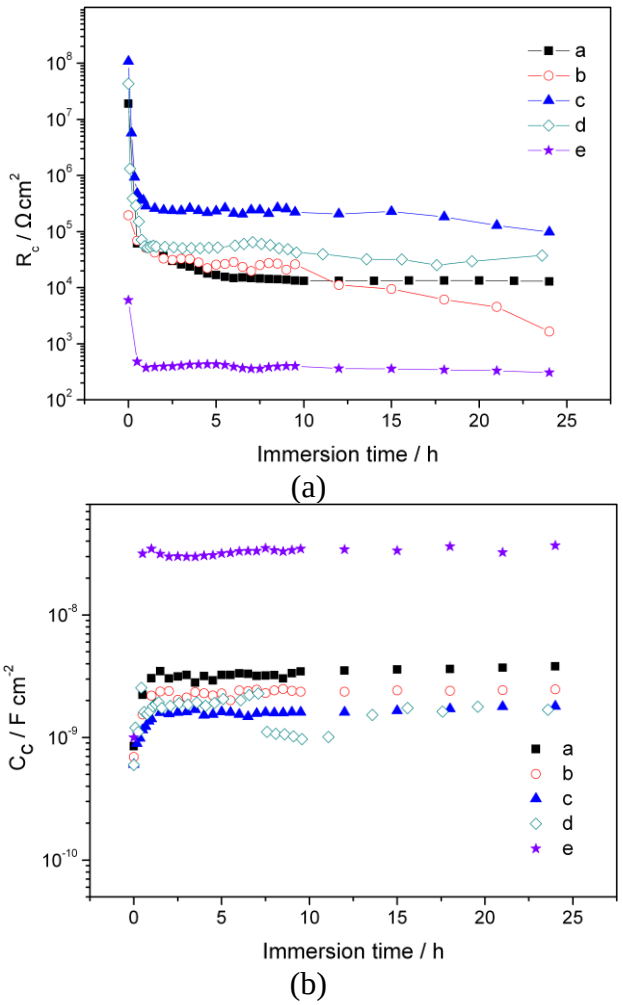


Figure 4. Evolution of coating resistances and capacitances of the UV-treated epoxy coatings (543 hours of irradiation) with different LMPAR/DGEBA molar ratios: a) 0.221, b) 0.318, c) 0.415, d) 0.515, e) 0.613.

The variation in the coating resistances and capacitances of the different epoxy samples with UV treatment for 543 hours is shown in Figure 4. It was found that all the coating resistances decreased dramatically after a very short immersion time and then maintained relatively stable values, which varied with the LMPAR/DGEBA molar ratio. As the ratio increased from 0.221 to 0.613, the coating resistances first increased and then decreased. The maximum resistance of the initial coating was observed in the sample, with a molar ratio of 0.415. As shown in Figure-4b, it is obvious that the constant capacitances of the coatings also varied with the LMPAR/DGEBA molar ratio. First, this constant decreased and reached a minimum for the molar ratio of 0.415, and then increased sharply with increasing irradiation time. In general, the coating capacitances were mainly related to the water uptakes. The sample with a LMPAR/DGEBA molar ratio of 0.415 exhibited better barrier properties.

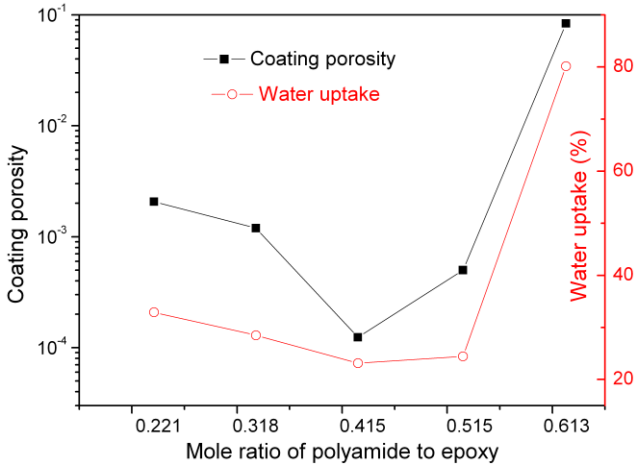


Figure 5. Variations in the coating porosity and water uptake at the saturation state during immersion as a function of the LMPAR/DGEBA molar ratio after 543 hours of UV irradiation.

To understand the water resistance of the epoxy resin, the coating porosity and water uptake were calculated from the EIS results. The porosity can be calculated as follows[22,23]:

$$P = \frac{d/A\kappa}{R_c} \quad (1)$$

where, *d* is the thickness of the sample, *A* is the electrode area, κ is the conductivity of the electrolyte, and R_c is the resistance of the coating.

The water uptake can be evaluated from the capacitance of the membrane by the following equation [24]:

$$\varphi(t) = \frac{\lg(C_t/C_0)}{\lg 80} \quad (2)$$

where, C_0, and C_t are the capacitance of the dry coating and the coating immersed for a period of t, respectively, while the constant 80 is the relative permittivity of water at 25 ^oC.

Therefore the water uptake and the porosity of the epoxy coatings can be calculated from equation(1) and (2). As shown in Figure 5, with the increasing LMPAR/DGEBA molar ratio, the variations in the water uptake and the porosity of the epoxy coatings with 543 hours of UV-treatment were very similar, suggesting that the results obtained from the two different methods are consistent. As the molar ratio increased from 0.221 to 0.415, the water uptake decreased from 32.90% to 23.12%, and the apparent coating porosity also decreased from 2.07 $\times 10^{-3}$ to 1.24 $\times 10^{-4}$. Then, the water uptake and the coating porosity increased to 80.14% and 8.38 $\times 10^{-2}$, respectively, as the dosage ratio increased rapidly to 0.613. Hence, considering the fact that the low water uptake was due to less degradation of the coatings, the optimal LMPAR/DGEBA molar ratio was approximately 0.415. These results were also consistent with the impedance modulus values (Figures 1-3). In addition, when the curing agent ratio was lower than 0.415, the water uptake and the porosity of the UV-treated epoxy coatings were relatively high, and the EIS spectra showed the characteristics of microporous structures. While the molar ratio was higher than 0.415, the water uptake and the coating porosity increased rapidly, and the EIS data revealed an interfacial corrosion feature.

4. CONCLUSION

The photodegradation behaviors were investigated for various epoxy-polyamide coatings upon UV irradiation. During the early stage of UV irradiation (88 hours), the low frequency impedance of the irradiated coating was higher than that of the as-prepared one without UV treatment, which confirms the existence of a post-curing process. With increasing irradiation time, the modulus decreased, and some micro-defects were generated near the sample surface. With UV irradiation for 543 hours, the lower modulus values and the emergence of a second time constant imply that the interfacial corrosion reaction of the coating occurred. The results indicate that the molar ratio of the curing agent plays a key role in the water resistance of the aged epoxy coating after a long immersion time in a NaCl solution. The optimal LMPAR/DGEBA molar ratio was approximately 0.415, when the water uptake and the porosity of the epoxy coating were relatively low, and the EIS spectra show the characteristics of highly cross-linked structures. When the curing agent ratio was lower or higher than 0.415, the water uptake and the coating porosity increased, and the EIS data revealed the formation of micropores or the appearance of an interfacial corrosion in the epoxy coating upon UV irradiation. Introducing LMAPAR in epoxy resin improves not only the anti-UV ageing effect, but also the water resistance of the coating during the degradation process.

ACKNOWLEDGEMENTS
This work was financially supported by the National Natural Science Foundation of China (No. 21174108) and the Large Scale Instrument and Equipment Sharing Foundation of Wuhan University (No. LF20170857).

References

1. X. Wang, L.L. Mao, M. Luo, P.F. Fang, Y.Q. Dai and K.M. Liew, *Prog. Org. Coat.*, 67(2010) 398.
2. M. Costa, G. Viana, L.F.M. da Silva and R.D.S.G. Campilho, *J. Adhesion*, 93 (2017) 127.
3. W.J. Zhang, G. Camino and R.J. Yang, *Prog. Polym. Sci.*, 67 (2017) 77.
4. V.B. Moller, K. Dam-Johansen, S.M. Frankaer and S. Kiil, *J. Coat. Technol. Res.*, 14 (2017) 279.
5. Z. Chen, C. Yin, S. Wang, Q.M. Fu, Q.R. Deng, Z.D. Lin, P. Fu, Y. Zhang, J.Y. Wu and P.F. Fang, *Polym. Adv. Technol.* 27 (2016) 1446.
6. Y. Malajati, S. Therias, J-L. Gardette, *Polym. Degrad. Stab.*, 96 (2001) 144.
7. B. Dao, J. Hodgkin, J. Krstina, J. Mardel, W. Tian, *J. Appl. Polym. Sci. 102 (2006) 3221*.
8. P. Musto, G. Ragosta, P. Russo, L. Mascia, *Macromol. Chem. Phy.*, 202 (2001) 3445.
9. C. Bockenheimer, D. Fata, W. Possart, *J. Appl. Polym. Sci.*, 91 (2004) 361.
10. A. Cherdoud-chihani, M. Mouzali, M.J.M. Abadie, *J. Appl. Polym. Sci.*, 69 (1998) 1167.
11. Z. Wang, F.W. Liu, J.J. Li, C.Q. He, X.Y. Peng, Z. Huang and P.F. Fang, *Acta Phys. Pol. A*, 132 (2017) 1523.
12. C.L. Chen, Y. He, G.Q. Xiao, Y.Q. Xia, H.J. Li and Z. He, *Appl. Surf. Sci.*, 444(2018) 511.
13. F. Ahmad, E.S.B. Zulkurnain, S. Ullah and N. Amir, *J. Anal. Appl. Pyrol.*, 132(2018) 171
14. C. Yin, S. Wang, Y.J. Zhang, Z. Chen, Z.D. Lin, P, Fu and L. Yao, *Environ. Sci.: Water Res. Technol.*, 3(2017) 1037.
15. X. Yuan, Z.F. Yue, X. Chen, S.F. Wen and L. Li, *Prog. Org. Coat.*, 78(2015) 168.

16. Y.J. Zhang, Z. Chen, L. Yao, X. Wang, P. Fu and Z.D. Lin, *Mater. Res. Express* 5(2018) 045606.
17. Q.Z. Luo, Q. Huang, Z. Chen, L. Yao, P. Fu and Z.D. Lin, *Mater. Res. Express* 5(2018) 065507.
18. F. Liu, M. Yin, B. Xiong, F. Zheng, W. Mao, Z. Chen, C. He, X. Zhao and P. Fang, *Electrochim. Acta*, 133(2014) 283.
19. S.V. Asmussen, G.F. Arenas and C.L. Vallo, *Prog. Org. Coat.*, 88(2015) 220.
20. F.W. Liu, M. Yin, B. Xiong, F. Zheng, W. Mao, Z. Chen, C. He, X. Zhao and P. Fang, *JJAP Conf. Proc*. 2(2014) 011207.
21. F. Zheng, C.Q. He, P.F. Fang, J.G. Wang, B.Y. Xiong, K. Wang, F.W. Liu, X.Y. Peng, X.G. Xu and Z.H. Xu, *Appl. Surf. Sci.*, 283(2013) 327.
22. R.D. Armstrong and D. Wright, *Electrochim. Acta*, 38(1993) 1799.
23. R.D. Armstrong, A.T.A. Jenkins and B.W. Johnson, *Corros. Sci.* 37(1995) 1615.
24. D.M. Brasher and A.H. Kingsbury, *J. Appl. Chem.* 4(1954) 62.