

An Historical Perspective on the Electrochemical Aspects of Corrosion Protection by Paints

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Dating at back to 19th century, electrochemical processes have been considered regarding corrosion and passivity (1). The electrochemical role of paints also becomes apparent upon recognition that mass transport inhibition alone cannot explain the corrosion protective properties of paint (2).

Research and development of new corrosion protective paints use a number of electrochemical methods for identifying corrosion inhibiting mechanisms (3,4). Electrical resistance and membrane potentiometric analysis were used early in the century to characterize corrosion protection by organic paint coatings (5). Mayne and coworkers recognized that paint coatings protected metal from corrosion more by slowing the ionic transport than by acting as a water and oxygen barrier. Key to this understanding was the observation of different types of ionic transport occurring across paint (6-8). One type of ionic transport gives results in conductivity proportional to the ionic concentration (D) of the environment and a second that much lower conductivity depends inversely (I) on concentration of the ionic environment. The first ionic transport occurs in virtual pores or pores while the second entails ionic movement through the polymer matrix.

Researchers began using ac concepts to understand electrochemical kinetics as early as the end of the 19th century (9). Some of the first ac electrical analyses of paint, however, were performed in the mid 20th century (10) but came into much broader use by the late 1970s particularly after I. Epelboin and his students introduced the transfer function analyzer to the corrosion community(11). Observation of the frequency dependence of organic films on steel (12,13) lead to the familiar pore resistance model where the pore resistance is attributed to the D form of ionic transport (13). By the end of the 1970s the importance of coating heterogeneity to corrosion mechanism was well established.

Often initiating from initial heterogeneities, anodic and cathodic electrochemical reactions on polymer coated or painted steel and aluminum become separated and contribute to degradation processes such as filiform corrosion and cathodic disbonding. Observation of the electrochemical reactions started from visual observations and then micro-electrochemical resistance probes. The methods were refined to continuous mapping by scanning electrochemical probes and electrochemical impedance

probes (14-16). Stratmann and his co-workers have most recently advanced this inquiry using the Kelvin probe to directly assess the electrochemical potential of the corroding polymer/metal interface (17).

Despite much progress in the use of electrochemical impedance and electrochemical noise (18,19), the goal of using a electrochemical method to predict coating life still remains. Nevertheless, electrochemical analysis has helped direct the mechanistic understanding of corrosion protection by paint and the development of paint and organic coatings over the last 100 years.

References

1. The electrochemical nature of corrosion has been first attributed to an anonymous paper by L. J. Thénard and R. Mallet appearing in 1819. H. Davy recognized the electrochemical aspect of corrosion suggesting galvanic protection of Cu sheathing of canal boats as early as 1824. Davy's student, M. Faraday was also an early proponent of the electrochemical aspect of corrosion (J. W. Mellor, "Inorganic and Theoretical Chemistry", vol 13, part 2, p 412, Wiley, 1961).
2. J. E. O. Mayne, Official Digest, 24, 127 (1952).
3. H. Leidheiser, Jr. "Electrical and Electrochemical Measurements as Predictors of Corrosion at the Metal-Organic Interface" in 'Corrosion Control by Coatings', Science Press, 1979
4. G. W. Walter, Corros. Sci., 26(1), 27 (1986)
5. J. K. Wirth as referenced by H. Leidheiser in ref.
6. C.C. Maitland and J. E. O. Mayne, Official Digest, 34, 972 (1962)
7. J. E. O. Mayne and J. D. Scantlebury, Br. Polymer J.2, 240 (1970)
8. J. E. O. Mayne and D. J. Mills, JOCCA, 58 , 155 (1975).
9. E. Warburg Wied. Ann., 67, 493 (1899)
10. D. Brasher and A. Kingsbury, J. Appl. Chem., 4, 62 (1954)
11. L. Beaunier, I. Epelboin, J. C. Lestrade, H. Takenouti, Surf. Technol.,4(3), 237 (1976).
12. G. Menges and W. Schneider, Kunststofftechnik, 12(11), 316 (1973).
13. M. Kendig and H. Leidheiser, J. Electrochem. Soc., 123, 982 (1976).
14. H. Isaacs and M. Kendig, Corrosion,36(6),269 (1980)
15. J. Standish and H. Leidheiser, Corrosion,36(8), 390 (1980).
16. Wittmann, MW; Leggat, RB; Taylor, SR, J. Electrochem. Soc.,146, 4071 (1999)
17. W. Furbeth and M. Stratmann, Prog. Org. Coating, 39, 23 (2000).
18. F. Mansfeld, C. C. Lee and G. Zhang, Electrochimica Acta , 1998 , 43(3-4)435 (1998).
19. Q. Le Thu, G. Bierwagen, S. Touzain, Prog. Org. Coating, 42, 179 (2001).