APPLICATIONS OF ELECTROCHEMICAL NOISE MEASUREMENTS IN CORROSION STUDIES: A REVIEW

C. Jeyaprabha, S. Muralidharan, G. Venkatachari and M. Raghavan

Central Electrochemical Research Institute,
Karaikudi - 630 006, India
Email: sileu@cscecri.ren.nic.in

ABSTRACT

This review summarizes the applications of electrochemical noise measurements in various corrosion processes like stress corrosion cracking, corrosion inhibitor evaluation, pitting corrosion and evaluation of organic coating

1. INTRODUCTION

In recent years, the application of electrochemical noise analysis (ECN) in corrosion and electrochemical studies has gained considerable interest even though this technique was introduced more than twenty years ago /1,2/. This method is non-perturbative and is found to give useful information about the nature of corrosion processes from the measurements of spontaneous current and potential fluctuations of the system. The low cost of the equipment and the ease of data collections have made this technique more attractive. Earlier reviews /3,4,5/ dealt very briefly with the applications of noise analysis in corrosion and passivation. Bertocci *et al.* /6/ described the types of noise, experimental methods used for measurements and schemes for analysis. An international symposium on electrochemical noise measurements for corrosion applications was conducted by ASTM in 1994 at Montreal /7/. The theoretical basis of noise measurements for corrosion studies has been discussed by Cotis *et al.* /8 /.

2. NOISE SOURCES /9 /

The possible sources of voltage and current generation of electrochemical systems are summarized below:

(i) Kinetics of exchange of atoms with sites on the surface (equivalent to Johnson's noise in the interfacial impedance)
(ii) Formation and detachment of bubbles
(iii) Fluctuations in rate of mass transport
(iv) Temperature fluctuations
(v) Occurrence of events controlled by nucleation, growth and death process (pitting)
(vi) Dielectric film breakdown process

3. METHODOLOGY /10, 11, 12 /

The method of noise analysis involves the measurement of fluctuations of current flowing between two identical electrodes kept at the same potential by means of zero resistance ammeter and measuring at the same time their voltage fluctuations with respect to a reference electrode. In some cases, the voltage measurements can also be carried out on a couple of electrodes identical to those employed in current measurements. From the voltage and current noise data the quantities like noise power, noise resistance and the spectral noise resistance values are obtained.

i) Noise power $\left(\bar{v}^2\right)$

The noise power value is obtained from the autocorrelation function of voltage - time data at $\tau = 0$. The auto correlation function is defined as

$$\phi_{xx}(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_0^{\infty} x(t).\, x(t+\tau)$$

where T is the total duration of measurement and τ is the delay time.

ii) Noise resistance, (R_n)

From the standard deviation of potential (σ v (t)) and current (σ i (t)), noise values, the noise resistance is obtained from the following relationship

$$R_n = \frac{(\sigma v(t))}{(\sigma i(t))}$$

iii) Spectral Noise Resistance R^o_{sn}

Fast Fourier transform (FFT) of the voltage and current noise data from the time domain to the frequency domain gives the frequency dependent of noise data. Normally the frequency range for which the FFT is carried out is 1mHz to 1Hz. The spectral noise plots which are similar to impedance plots can be obtained from the relationship

$$R_{sn}(f) = \frac{|V_{FFT}(f)|}{|I_{FFT}(f)|}$$

where, V_{FFT} (f) and I_{FFT} (f) are the FFTs of potential and current fluctuations. The plot of log R_{sn} vs log f is similar to the impedance plot and the spectral noise resistance R^o_{sn} is given by

$$R^o_{sn} = \lim_{f \to 0} \left[R_{sn} f(t) \right]$$

In some cases $R_{sn}{}^{\circ}$ is related to R_n or R_p as

$R_{sn}[0] = R_n = R_p$;

Some authors /13-16/ have used the maximum entropy method (MEM) instead of the FFT method for frequency domain transformation of time domain voltage and current noise data. It is stated that MEM has the following advantages over FFT

i) it is faster than FFT because it does not require ensemble averaging

ii) it gives smoother spectra than the FFT
iii) it allows computation of the spectrum at frequency lower than the inverse of acquisition time, which is the lowest frequency, calculated by FFT.

Roberge *et al.* /17/ have used rescaled sample analysis (R/S) and the stochastic process detector (SPD) techniques for noise analysis. The amplitude of potential noise and current noise signals are usually less than 10^{-3} volts and 10^{-6} amperes respectively. The frequency of interest for electrochemical noise is generally lower, i.e. 0.001 Hz to 1 Hz. Pictorius /18/ has evaluated the choice of electrode size in ECN measurements and the sampling rate.

4. APPLICATIONS OF NOISE ANALYSIS

4.1. Stress Corrosion Cracking (SCC)

Earlier works of Hoar /19/ showed that there is considerable current flow accompanied by cracking. Loto *et al.* /20/ studied the electrochemical noise generated during stress corrosion cracking of α-brass in Mattson solution and analyzed the noise data using MEM. They found that cracking in most cases gave the highest noise amplitudes as well as the highest standard deviation values. The noise amplitude and the role of slopes could be related to the different electrochemical processes occurring during SCC. They obtained similar results for an aluminium alloy in 3.5 % NaCl solution /21/ and for a high strength steel in 3.5% NaCl containing 500ppm of H_2S /22/

Wells *et al.* /23/ studied the SCC of sensitized stainless steel in dilute thiosulphate at room temperature and in high purity oxygenated water at high temperature /24/ using slow strain rate test technique. In both cases current pulses were associated with initiation of IGSCC and crack jump from one grain boundary to the next.

Hickling *et al.* /25/ investigated the use of electrochemical noise to detect SCC initiation of 304 stainless steel in simulated BWR environments. They found that the standard deviation of electrochemical potential proved to be the best indication of SCC initiation but the degree of correlation depended upon both periodicity of calculation and the electrode configuration. It was further shown that once advancing crack becomes deep and moved away from the surface, the noise signal accessible outside the crack becomes small. A study /26/ has been made on the measurement of potentiostatic electrochemical noise for Cu_3Au polycrystals over the whole duration of slow strain rate tensile tests up to brittle cracking in acidic sulphate medium.

4.2 Corrosion Inhibition

Electrochemical noise recording can be carried out at high sampling rate and hence ECN may be able to monitor rapidly changing corrosion inhibitor film formation of breakdown process. Electrochemical noise analysis was used to monitor the effectiveness of inhibitor by continuous and batch treatment against CO_2 corrosion in oil fields /27,28/. It was shown that ENA was able to monitor effectively the formation and deterioration of inhibitor film: as the inhibitor film formed, the current noise amplitude decreased rapidly and the noise resistance R_n was found to increase sharply. Conversely, the current noise amplitude increased rapidly during deterioration of inhibitor film and R_n decreased rapidly. Further, it was found that R_n variation was similar to R_p variation

The use of organic inhibitors to inhibit crevice corrosion of copper in NaCl solution was examined by ECN analysis /29/. The performance of inhibitors for AA6351 aluminium alloy in 0.5M chloride solutions has been studied by measuring the noise power values from the corrosion potential fluctuations /30/.

4.3 Corrosion Monitoring

Eden *et al.* /31/ found that a noise resistance $R_n = \sigma_v / \sigma_i$ which can be deduced from voltage and current noise data, where σ_v and σ_I are the standard deviations of voltage and current noise respectively, is similar to the polarization resistance R_p and can be used to calculate the corrosion rate. Chen *et al.* /32/ showed that the corrosion rates of low carbon steel in 0.1M citric acid and 0.05M H_2SO_4 obtained from the ENA method compared very well with the results of LPR technique. Based on the ECN method, a noise detection unit was developed for continuous monitoring of corrosion rate in a chemical plant /33/. The use of this unit was demonstrated by measuring corrosion rate of duplex SS and CrNiMoTi steel. Monticelli *et al.* /34/ applied the ECN analysis to monitor copper corrosion rates in solutions of industrial waters.

4.4. High Temperature Oxidation

Farrel *et al.* /35/ have used the ECN method for the evaluation of hot corrosion of nickel based alloys in sulphates and sulphate-chloride melt. Bottomley *et al.* /36/ have examined the use of noise analysis in corrosion studies of nickel and Ni20Cr alloy in molten Na_2SO_4 - NaCl at 700°C to 950°C. The nickel metal current noise amplitude in sodium chloride melts is high compared to Na_2SO_4 melts indicating a more disrupted scale in chloride containing melts. Further, the current noise variation rises sharply with temperature up to the melting point and then a fall is observed which is coincident with the fall in solution resistance (R_s) and R_{ct} values to lower steady values indicative of corrosion.

The oxidation behaviour of iron in $NaNO_3$ - $NaNO_2$ melt in the presence and absence of chloride ions was studied by ECN technique /37-39/. It was found that voltage fluctuations and electrochemical noise power were decreasing with immersion time due to growth of compact oxide film. This trend was maintained even after the addition of 2% NaCl. However, a rapid increase of noise power was observed after the addition of 3% NaCl due to breakdown of oxide film.

4.5 Pitting Corrosion

ECN measurements permitted the study of spontaneous behaviour of the specimens without controlling electrochemical variables and hence pitting corrosion could be studied quantitatively. The pitting corrosion behaviour of 304 stainless steel in solution of Cl^- and $S_2O_3^{2-}$ has been studied by ECN measurements and found that the Cl^- - $S_2O_3^{2-}$ mixture could provoke spontaneous pitting even at ambient temperature /17/.

Roberge *et al.* /40, 41/ studied the pitting corrosion of 7039-T64 and 2519 aluminium alloys in 3% NaCl by ECN and EIS methods. A correlation between noise data and the degree of pitting was found. The slope of the voltage fluctuation was correlated with the pitting tendency of Al alloys. A higher slope is indicative of more resistance to pitting corrosion.

Several studies have reported that noise analysis can be used /42 - 44/ to distinguish between pitting corrosion from the roll-off of voltage noise amplitude of the corroding electrodes. In these studies a roll-off of 20dB $decade^{-1}$ was thus associated with pitting attack while one of 40dB $decade^{-1}$ was found to be more characteristic of general corrosion processes.

Yang *et al.* /45/ have shown that ECN measurements can serve as a useful tool to distinguish between pitting corrosion and crevice corrosion by studying the ECN behaviour of carbon steel in bicarbonate solutions containing chloride since the potential and current fluctuations of pitting corrosion are evidently different from that of the crevice corrosion.

Liu *et al.* /46/ have used the ECN method to monitor the corrosion of metals and alloys in contact with heat transporting fluid. ECN was measured as a function of oxygen concentration, flow rate, temperature and pressure in simulated heat transport circuit fluids at temperature up to 550°C and at pressure as high as 276bar. They showed that the magnitude of noise was sensitive to change in the chemical and physical properties of the fluid.

Using noise power measurements /47-49/, the pitting corrosion of steel in inhibitor solutions containing chloride and H20, aluminium and 304 SS in NaCl solutions has been studied. It is reported that the noise power is found to be increased by 100 to 1000 times during pitting corrosion of metals.

Smith *et al.* /50/ found that the electrochemical current noise could characterize the carbon film bearing copper tubes with respect to their ability to undergo pitting corrosion. Cheng *et al.* /51/ studied the feature of electrochemical noise during pitting corrosion of carbon steel in chloride solutions containing inhibitors. Noise analysis in the frequency domain showed that pitting initiation was characterized by the slope of the PSD plot approaching -2 and extending the immersion time decreased the pitting initiation rate, as indicated by the decreased PSD slope and increased PSD frequency.

Gusmano *et al.* /52/ studied the pitting corrosion behaviour of steel in Na_3PO_4 solution containing chloride. It was found that σ values of current of ≤ 0.5nA and σ value of potential $\leq 50\mu$V were observed in the passive state. Besides, a roll of ≤20dB / decade in the potential PSD was obtained for pitting attack. There was good correlation between R_n with R_p values obtained by LPR

Bertocci /53/ derived impedance plots for the voltage and current noise spectrum recorded on copper electrodes immersed in a copper sulphate / sulphuric acid solution. Extensive studies carried out on the breakdown of passive film by chloride ions revealed that the generation of white noise during the passive film formation and low frequency flicker type noise during breakdown of passive film /54, 55/. Further, the current noise measurements revealed the nature of pitting and the repassivation of pits /56/.

Suter *et al.* /57/ studied the effect of MnS inclusions in stainless steel on pitting corrosion by ECN method. The results showed that the pitting potentials depend on the inclusion size and the inclusion size must be kept below 1 micrometer to improve substantially the pitting resistance of stainless steel.

The corrosion behaviour of AA 6061 and AA 2014 metal matrix composites reinforced with alumina particles during exposure to 0.1 M NaCl solution was studied by Monticelli *et al.* /58/. The power spectrum density plots exhibited 1 / f (α) trends with alpha values around 20 dB / decade during pitting corrosion while the values tended to zero during general corrosion.

Williams *et al.* /59/ studied the pitting initiation of 304L stainless steel in NaCl solutions from current noise measurements. The pitting frequency depended on the potential. The current - time signature of pitting events are either current increasing linearly with time or current increasing as $\sqrt{t}$.

ECN analysis is used for the evaluation of crevice corrosion of AISI 430 stainless steel in 3 % sodium chloride. A crevice former was used in order to induce a crevice corrosion attack. Current and potential noise signals were simultaneously recorded and the noise resistance was determined /60/.

4.6. Evaluation of Coatings

In recent years ECN measurements have been used for evaluation of performance of coatings. The standard deviation of potential σ [v (t)] and current σ [i (t)] noise fluctuations are followed as a function of time to detect the initiation of coating damage and corrosion of substrate. Generally it has been reported that σ [v (t)] decreases and σ [i (t)] increases as the coatings degrade.

Skerry *et al.* /61-63/ have used this technique for evaluation of coatings and suggested that the noise resistance (R_n) obtained by statistical analysis of experimental data in the time domain could be related to the dc limit of impedance. By measuring the potential noise, Metikes *et al.* /64/ have shown that the amplitude spectra of low frequency electrochemical potential noise correlates the performance of coatings. Mills *et al.* /65-68/ have evaluated the polymer coatings by R_n measurements. In these studies they obtained a definite relationship between R_n and coating degradation and their R_n data allowed different coatings systems to be ranked as good, fair and poor grades.

Mansfeld and coworkers /69-73/ have analyzed the noise data in the frequency domain and calculated the spectral noise resistance R_{sn} (f). They have shown that the spectral noise plots that are the ratio of FFT of potential and current fluctuations at each frequency are similar to the impedance plot and extrapolation to a DC limit allows the determination of spectral noise resistance R_{sn}° (f). Using this method they evaluated the performance of different coating systems exposed to natural seawater, river water and artificial seawater /74 -76/. They have shown that the ECN method has great potential to monitor the performance of a coating, but information regarding the coating capacitance and its changes with time due to water uptake cannot be obtained by ECN measurements.

Wain *et al.* /77/ have derived a simple circuit for the measurement of electrochemical noise for the evaluation of coatings on museum artifacts. They have found that the ECN method can be used for checking the coating quality quickly by measuring σ v, σ i and R_n.

Recently Mills *et al.* /78/ have studied the performance of coatings with defects by ECN method. They have found that R_n values give a quantitative indication of performance of coating and have good correlation with impedance values. The effectiveness of chemical treatment for prevention of staining on 6061 aluminium alloys in humid atmosphere has been carried out by measuring the noise power values /79/.

Various novel methods for ECN measurements of coated steel and detached film have been described /80/. The results were compared with the values obtained by DC resistance measurements. ECN method has been used to optimize the coating of thin aluminium coating on mild steel /81/

The application of electrochemical impedance spectroscopy (EIS) and ECN methods for the determination of the rate of corrosion of under paint corrosion process has been demonstrated /82/.

The degradation process of polyurethane coatings on steel subjected to slurry erosion-corrosion has been studied by measuring current noise /83/. Analysis of current noise data indicated the coating degradation process. Further the skewness and PSD slope indicated the initial stages of coating degradation.

The performance of plasma polymerized films as pretreatment for cold rolled steel were studied by electrochemical impedance spectroscopy and electrochemical noise measurements /84/.

5.0 CONCLUSION

Measurement of ECN is capable of distinguishing pitting corrosion and uniform corrosion. Further it is also possible to monitor the degradation of organic coatings, the performance of inhibitor and the initiation of stress corrosion cracking by measuring voltage and current noise.

ACKNOWLEDGEMENT

One of the authors, Miss C. Jeyaprabha, thanks the Council of Scientific and Industrial Research, New Delhi, India, for the award of a Senior Research Fellowship.

REFERENCES

1. W.P. Iverson, *J.Electrochem.Soc.*, **115**, 617 (1968).
2. V.A. Tyagai, *Electrochim.Acta.*, **16**, 1647 (1971).
3. K. Tachibana and G. Okamoto, *Rev.Coatings and Corrosion.*, **4**, 229 (1981).
4. C. Gabrielli and M. Keddam, *Corrosion.*, **48**, 794 (1992).
5. C. Gabrielli, F. Huet, M. Keddam and R. Oltra, *Corrosion.*, **46**, 266 (1990).
6. U. Bertocci and F. Huet, *Corrosion.*, **51**, 131 (1995).
7. Proceedings of conference on electrochemical noise for corrosion applications, *ASTM, **STP***, 1277 (1996).
8. R.A. Cottis and S. Turgoose, *Mat.Sci.Forum.*, 192 - 194, 663 (1995).
9. D.E. Williams in *Electrochemical Corrosion Testing,* Ed. E. Heitz, J.C.Rowlands and F.Mansfeld., **101**, 253 (1986).
10. F. Mansfeld, L.T. Han, C.C. Lee, C. Chen, G. Zhang and H.Xiao, *Corr.Sci.*, **39**, 255 (1997).
11. U. Bertocci, C. Gabrielli, F. Huet and M. Keddam, *J.Electrochem.Soc.*, **144**, 31, 37 (1997).
12. Gordon P. Bierwagen, *J.Electrochem.Soc.*, **141**, L155 (1994).
13. J.C. Uruchurtu and J.L. Dawson, *Corrosion.*, **43**, 19 (1987).
14. P.C. Searson and J.L. Dawson, *J.Electrochem.Soc.*, **135**, 1908 (1988).
15. F. Mansfeld and H. Xiao, *J.Electrochem.Soc.*, **140**, 2205 (1993).

16. U. Bertocci, J. Frydman, C. Gabrielli, F. Huet and M. Keddam, *J.Electrochem.Soc.*, **145**, 2780 (1998).
17. P.R. Roberge, S. Wang and R. Roberge, *Corrosion.*, **52**, 733 (1996).
18. P.C. Pictorius, *Corrosion.*, **53**, 273 (1997).
19. T.P. Hoar and J.G. Hines, *J. Iron and Steel Inst.*, **182**, 24 (1956).
20. C.A. Loto and R.A. Cottis, *Corrosion.*, **43**, 499 (1987).
21. C.A. Loto and R.A. Cottis, *Corrosion.*, **45**, 136 (1989).
22. C.A. Loto and R.A. Cottis, *Corrosion.*, **46**, 12 (1990).
23. D.B. Wells, J. Stewart, R. Davidson, P.M. Scott and D.E. Williams, *Corr.Sci.*, **33**, 39(1992).
24. J. Stewart, D.B. Wells, P.M. Scott and D.E. Williams, *Corr.Sci.*, **33**, 73 (1992).
25. J. Hickling, D.F. Taylor and P.L. Andreson, *Materials and Corrosion.*, **49**, 651 (1998).
26. B. Malki, A. Legris, J.L. Pastol and D. Gorse, *J.Electrochem.Soc.*, **146**, 3702 (1999).
27. Y.J. Tan, S. Bailey and B. Kinsella, *Corr.Sci.*, **38**, 1681 (1996).
28. Y.J. Tan, B. Kinsella, and S. Bailey, *Br.Corr.J.*, **32**, 212 (1997).
29. C. Monticelli, M.C. Boggiani and F. Zuchi, *Proc.of 8th European Symp on Corrosion Inhibitors*, Ferrara, 1995.
30. C. Monticelli, G. Brunoro, A. Frignani and G. Trabanelli, *J. Electrochem. Soc.*, **139**, 706 (1992).
31. D.A. Eden, K. Hladky, D.G. John and J.L. Dawson, *Proc. Conf. Corrosion '86*, Houston, TX, USA - March 1986, NACE paper 274.
32. J.F. Chen and W.F. Bogaerts, *Corrosion*, **52**, 753 (1996).
33. H. Leonhard, F. Stoll and R. Dölling, *Materials and Corrosion.*, **49**, 684 (1998).
34. C. Monticelli, G. Trabanelli and G. Meszaros, . *J.Appl.Electrochem.*, **28**, 963 (1998).
35. D.M. Farrel, W.M. Cox, F.H. Stott, D.A. Eden, J.L. Dawson and G.C. Wood, *High Temp.Technol.*, **3**, 15 (1985).
36. P.D.W. Bottomley, J.R. Gill and J.L. Dawson, *Mat.Sci.Forum.*, **8**, 509 (1986).
37. I.B. Singh and G. Venkatachari, *Indian J.Chem.Tech.*, **4**,163 (1997).
38. I.B. Singh, G. Venkatachari and K. Balakrishnan, *Corr.Sci.*, **36**, 1777 (1994).
39. I.B. Singh, G. Venkatachari and K. Balakrishnan, *Proc 12th ICC*, (Houston, TX, USA) **12**, 979 (1993).

40. P.R. Roberge, E.Halliop, D.R. Lenard and J.C. Moores, *Corr.Sci.*, **35**, 213 (1993).
41. P.R. Roberge and D.R. Lenard, *J.Appl.Electrochem.*, **28**, 405 (1998).
42. K. Hladky and J.L. Dawson, *Corr.Sci.*, **21**, 317 (1981).
43. J. Uruchurtu and J.L. Dawson, *Mat.Sci.Forum.*, **8**, 113 (1986).
44. P.C. Searson and J.L. Dawson, *J.Electrochem.Soc.*, **135**, 1908 (1988).
45. M.Z. Yang, M. Wilmott and J.L. Luo, *Corrosion.*, **54**, 869 (1998).
46. C. Liu, D.D. Macdonald, E. Medina, J.J. Villa and J.M. Beuno, *Corrosion.*, **50**, 687 (1994).
47. S. Muralidharan, S.P. Manoharan, G. Venkatachari and K. Balakrishnan, *B. Electrochem.*, **6**, 4 (1990).
48. S.P. Manoharan, S. Muralidharan, G. Venkatachari and K. Balakrishnan, *Proc.11th ICC*, Florence, Italy, **1**,541 (1990).
49. S. Muralidharan, G. Venkatachari and K. Balakrishnan, *Proc.12th ICC*, NACE, **3A**, 1403 (1993).
50. S. Smith and R. Francis, *Br.Corros. J.*, **25**, 285 (1990).
51. Y.F. Cheng, B.R. Rairdan and J.L. Luo, *J.Appl.Electrochem.*, **28**, 1371 (1998).
52. G. Gusmano, G. Montesperelli, S. Pacetti, A. Petitti and A.D' Amico, *Corrosion.*, **53**, 860 (1997).
53. U. Bertocci, *J.Electrochem.Soc.*, **127**, 1931 (1980).
54. K. Nachstedt and K.E. Heusler, *Electrochim. Acta.*, **33**, 311 (1988).
55. F. Flis, J.L. Dawson, J. Gill and G.C. Wood, *Corr.Sci.*, **32**, 877 (1991).
56. C. Garbrielli, F. Huet and M. Keddam, *J.Appl.Electrochem.*, **15**, 503 (1985).
57. T. Suter and H. Bohni, *Electrochim.Acta.*, **42**, 3275 (1997).
58. C. Monticelli, F. Zucchi, G. Brunoro and G. Trabanelli, *J. Appl. Electrochem.*, **27**, 325 (1997).
59. D.E. Williams, M. Fleischmann, J. Stewart and T. Brooks, *Mat. Sci. Forum.*, **8**, 151 (1986).
60. G. Gusmano, F. Marchioni, and G. Montesperelli, *Materials and Corrosion.*, **51**, 537 (2000).
61. B.S. Skerry and D.A. Eden, *Prog.Org.Coat.*, **15**, 269 (1987).
62. C.T. Chen and B.S. Skerry, *Corrosion.*, **47**, 598 (1991).
63. M. Moon and B.S. Skerry, *J.Coat.Tech.*, **67**, 35 (1995).
64. M. Metikos-Hukovic, M. Loncar and G. Zevnik, *Materials and Corrosion.*, **40**, 494 (1989).
65. D.J. Mills, , B. Skerry and D.Tallman, *Proc. 12th ICC.*, **1**, 182 (1993).

66. D.J. Mills, G.P. Bierwagen, B.S. Skerry and D. Tallman., *Mater.Perform.*, **34**, 33 (1995).
67. S.Mabbutt and D.J. Mills, *Surf.Coat.Int.*, **80**, 18 (1997).
68. D.J. Mills, G.P. Bierwagen, B.S. Skerry and D. Tallman, *Proc. 12th ICC.*, NACE, **1**, 194 (1993).
69. F. Mansfeld and H. Xiao, *Proc. 12th ICC.*, NACE, 1388 (1993).
70. H. Xiao and F. Mansfeld, *J.Electrochem.Soc.*, **141**, 2332 (1994).
71. F. Mansfeld and H. Xiao, *ASTM, STP 59,* 1277 (1996).
72. F. Mansfeld, *J.Appl.Electrochem.*, **25**, 187 (1995).
73. F. Mansfeld and H. Xiao, *J.Electrochem.Soc.*, **140**, 2205 (1993).
74. F. Mansfeld, L.T. Han and C.C. Lee, *J.Electrochem.Soc.*, **143**, L286 (1996).
75. F. Mansfeld, H. Xiao, C.C. Lee and L.T. Han, *Corrosion/ '95,*, Paper No.530, NACE (1995).
76. F. Mansfeld, C.C. Lee and G. Zhang, *Electrochim.Acta.*, **43**, 435 (1998).
77. A. Wain, J. Alvarez and T.H. Randle, *Proc.13th ICC*, Paper No. 126 (1997).
78. D.J. Mills and S. Mabbutt, *Prog.Org.Coat.*, **39**, 41 (2000).
79. G. Venkatachari, C. Marikkannu, S. Muralidharan and K. Balakrishnan, *B.Electrochem.*, **12**, 77 (1996).
80. S.J. Mabbutt and D.J. Mills, *Br.Corros.J.*, **33**, 158 (1998).
81. A. Burkert, A. Heyn, J. Gollner, I. Garz, E. Vera and G.K. Wolf, *Materialwiss Werkstofftech.*, **29**, 496 (1998).
82. B. Lengyel, L. Meszaros, G. Meszaros, E. Fekete, F. Janaszik and I. Szenes, *Prog.Org.Coat.*, **36**, 11 (1999).
83. Y. Puget, K. Trethewey and R.J.K. Wood, *Wear.*, **235**, 552 (1999).
84. K.D. Conners, W.U. Van Ooij, D.J. Mills and G.P. Bierwagen, *Br.Corros.J.*, **35**, 141 (2000).