

LETTER

Reply to comments by R. D. Armstrong and A. T. A. Jenkins on the paper 'Use of EIS for the study of corrosion protection by polymer coatings' by F. Mansfeld.*

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In considering Armstrong and Jenkins' (A&J) comments one needs first to remember that the model in Fig. 1 of the paper under discussion, which was used by Haruyama *et al.* [1] to derive the breakpoint frequency method, is based on the assumption that the coating resistivity, ρ , decreases with exposure time without formation of 'real' pores as those shown in A&J's comments (Fig. 1). This model can be applied to coatings with blisters where one obviously can not have 'real' pores. Later Hirayama and Haruyama [2] modified their model to include the effects of 'real' pores.

In using Equation 1, ρ should be the resistivity of the coating which is assumed to decrease with time. Since A&J used the resistivity of the electrolyte instead, their R_{po}^o is by far too low, resulting in a value of A_d which is also by far too low. The use of values of R_p^o and C_{dl}^o obtained for bare metals is problematic since the chemistry, current distribution, etc. are most likely to be quite different at the melt/coating interface from those in bulk solution. Since the true values of R_{po}^o , R_p^o and C_{dl}^o are usually unknown, it seems to be safer to evaluate the *relative* changes of A_d with time rather than attempting to calculate absolute values. In the paper under discussion, the changes of $D = A_d/A$ with time were plotted in Fig. 12 assuming $D = 10^{-4}$ after 32 days. Regardless of the shape of a pore the impedance measurement will always reflect the increase of A_d although it might not be possible to determine its accurate value.

The fact that, in general, Bode plots provide a much better overview of impedance spectra for polymer coated metals has been demonstrated convincingly in Fig. 2 of the paper under discussion. The spectrum provided by A&J is a special case, since R_{po} and the dc limit of the impedance are very similar and therefore the data can be presented in a linear plot. The experienced investigator will note in either plot that the impedance at low frequencies is apparently dominated by a transport process. A&J seem to have assumed that the low-frequency data can be modelled by a parallel $R-C$ combination. For data such as those shown in Figs 2 and 3 of A&J's comments, it is often quite difficult to obtain accurate values of C_{dl} and, therefore, of A_d with Boukamp's analysis software.

The value of Bode plots lies in the possibility to compare the frequency dependence of impedance spectra for experimental and fitted data. Only when the maxima and minima of the phase angle agree in both magnitude and frequency for both plots, can one assume that the fit has been carried out correctly.

References

- [1] S. Haruyama, M. Asari and T. Tsuru, in 'Corrosion Protection by Organic Coatings', Electrochemical Society, *Proceedings*, vol. 87-2 (1987) p. 197.
- [2] R. Hirayama and S. Haruyama, *Corrosion* **47** (1991) 952.