

A.C. IMPEDANCE — A TOOL FOR THE PAINT TECHNOLOGIST

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INTRODUCTION

Although a.c. impedance has come to prominence lately for studying anti-corrosive coatings, it is still eschewed by many paint technologists. At first sight this is surprising since the techniques are very versatile and, by modern standards, comparatively inexpensive. A possible explanation lies in the fact that most people responsible for the development and testing of paints are ungrounded in a.c. theory. Accordingly, this paper aims to broaden the appeal of impedance work by presenting, as simply as possible, some of the precepts of the art. It will be shown how impedance data are obtained for coated metal specimens and how attempts are made to interpret these data in terms of the coatings' performance.

Impedance

If an alternating voltage, V , of the form:
 $V = V_0 \sin(\omega t)$ (1)

where V_0 is the amplitude

ω is the angular frequency ($= 2\pi f$)

t is the time

is applied to a combination of passive components (resistors, capacitors, inductors) then the resulting current, i , will also be sinusoidal as is illustrated in Fig. 1.

$$i = i_0 \sin(\omega t + \phi) \quad (2)$$

where i_0 is the current amplitude

ϕ is the phase shift.

These two equations imply that, at a given time and frequency, the relationship between V and i is defined by the ratio of their amplitudes and the phase shift. This relationship is the IMPEDANCE Z . It is a vector quantity with a magnitude, or modulus, $|Z|$:

$$|Z| = V_0 / i_0 \quad (3)$$

and a direction, or argument, ϕ .

As with all vector quantities, it is convenient to resolve Z into its orthogonal components. This is done by using a complex plane (Argand) diagram wherein the real (Z') axis represents the in-phase component and the imaginary ($-jZ''$) axis represents that component which is out of phase by $+90^\circ$. Thus, instead of dealing with Z in terms of $|Z|$ and ϕ , it is more convenient to manipulate Z' and Z'' . Figure 1 shows the inter-relation of these parameters.

Complex number notation provides a useful format for writing down the REACTANCES of individual circuit components:

$$\begin{array}{lll} \text{Resistance} & Z' = R & Z'' = 0 \\ \text{Capacitance} & Z' = 0 & Z'' = 1/-j\omega C \\ \text{Inductance} & Z' = 0 & Z'' = j\omega L \end{array}$$

Where C is the capacitance (Farads)

L is the inductance (Henrys)

At a given frequency the total impedance of any combinations of such components may be calculated by summing the (vector) impedances in a manner which is directly analogous to that used for (scalar) resistances: *i.e.* for series circuits:

$$Z = Z_1 + Z_2 + \dots + Z_n \quad (4)$$

and for parallel circuits

$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} + \dots + \frac{1}{Z_n} \quad (5)$$

The techniques of handling complex numbers are very apt for this. Consider, for example, a single resistor R and capacitor C connected in series. The total capacitance is given by:

$$Z = R + \frac{1}{-j\omega C} \quad (6)$$

This may be represented on an extension of the Argand diagram known as a Nyquist plot (Fig. 2(a)). This shows the relationship between Z' and Z'' when the variable ω is eliminated. It represents the locus of the end points of the continuum of impedance vectors obtained by varying ω between 0 and ∞ .

If, on the other hand, a resistor and capacitor are connected in parallel, then the impedance is given by:

$$\frac{1}{Z} = \frac{1}{R} + \frac{1}{1/-j\omega C} \quad (7)$$

i.e.

$$Z = \frac{R}{1 - j\omega CR} \quad (8)$$

If (8) is multiplied above and below by $(1 + j\omega CR)$ then Z may be resolved into its components:

$$Z' = \frac{R}{1 + (\omega CR)^2} \quad \& \quad Z'' = \frac{\omega CR^2}{1 + (\omega CR)^2} \quad (9)$$

The form of the Nyquist plot for this parallel combination only becomes apparent when ω is eliminated between equations (9) to yield the relation between Z' and Z'' .

$$Z'^2 + Z''^2 - RZ' = 0 \quad (10)$$

This is the equation of a circle centred on the real axis at $+R/2$ and having a radius of $R/2$ (Fig. 2 (b)). Furthermore, if the expression for Z'' in (9) is optimised it is found that the maximum out of phase component occurs when:

$$\omega = 1/CR \quad (11)$$

and the product CR , which has units of seconds, is known as the TIME CONSTANT of the circuit.

The foregoing processes may be used to determine the multifrequency impedance spectrum of any network of components providing their individual reactances are known. Conversely, it is also possible, but much less straightforward to concoct a circuit to explain an experimentally determined impedance curve. In practice this latter procedure is complicated by the plurality of circuits which may be fitted to a given spectrum. Nevertheless, it is this activity which forms the nub of impedance studies on coated metals. However, before this topic is pursued it would be apposite to outline the manner in which impedance curves are acquired.

Impedance Measurement — The Frequency Response Analyser

The essential feature of any impedance measurement system is that it should impose a sinusoidal voltage (or current) signal upon the specimen and analyse the current (or voltage) response. The process is repeated over a range of frequencies and the variations of Z with ω is recorded. In the past a number of techniques have been employed including a.c. bridges, oscillographic methods and lock-in amplifiers. In general these have the disadvantages of being tedious to operate and incapable of dealing with frequencies below c.a. 10 Hz. Nowadays the trend is towards the digital frequency response analysers (FRA), which are also referred to as transfer function analysers (TFA). FRA's,

such as the Solartron 1250, have the major advantages that they can be fully automated under the control of microcomputers and can operate at low ($<1\text{mHz}$) frequencies.

The FRA consists of a programmable generator and a two channel analyser. The generator provides the stimulating waveform and the analyser performs a digital correlation between the voltage and current responses of the specimen. The resulting impedance information is fed via a digital communications bus to the controlling microcomputer which then, according to its program, resets the generator to the next frequency and the process is repeated.

There are a number of methods whereby the signal generated by the FRA is applied to the coated specimen. An electrochemical interface is required and, in common with all electrochemical measurements, contact of the specimen with a continuous electrolyte is needed. This contact is achieved either by immersing the test panel wholly within a tank, in which case careful attention must be exercised to ensure the masking of panel edges and connections, or else by affixing a test cell to the surface of a horizontal panel.

The nature of the electrochemical interface used depends upon whether it is desired to determine the impedance under conditions of controlled electrode potential, controlled current or, as in the case with the 2-electrode measurement described by Scantlebury and Ho¹, with neither parameter fixed. This latter arrangement is shown in Fig. 3. The test cell consists of the painted specimen and a counter electrode which may either be an identical panel or, more usually a low impedance probe (eg a large piece of Pt foil). The operational amplifier is wired in a current to voltage converter mode.

It can be shown from the properties of op-amps that, in this negative feedback arrangement:

$$Z_c = \frac{V_1}{V_2} \cdot R_{std} \quad (12)$$

where Z_c is the impedance of the cell which approximates to the impedance of the specimen if the resistance of the counter electrode is low.

This method is quite acceptable for polarising coatings which give essentially capacitive responses (see below). However, Callow and Scantlebury² have demonstrated that this arrangement is unsatisfactory for polarising defective coatings. They showed the advantage of using a 3-electrode potentiostatic arrangement whereby the perturbing signal is superimposed upon a fixed d.c. potential level. Walter³, on the other hand, has used a potentiostat wired in a galvanostatic mode.

Model Circuits

The study of coatings by a.c. impedance is an iterative procedure. A typical sequence is to measure the impedance spectrum, to devise a model circuit which reasonably fits the data and then to relate the individual model components with the putative properties of the metal-coating-electrolyte system. The sequence is repeated over a period of time. Alterations in the impedance necessitate modifications of the circuit which, in turn, are related to the changing properties of the system. The process continues with the circuits being revised in the light of experience. Ultimately the aim is to be able to relate the models to the mechanisms of protections and to employ the technique as a predictor of coating performance.

Naturally the question arises as to what types of circuits are most applicable. There can, of course, be no single answer since the variations in coating types, and conditions, are essentially infinite. It is beyond the scope of this paper to provide a critique of

the various models advanced in the literature; for which the reader may be directed to a recent review by Szauer⁸. Instead it will suffice to illustrate the thinking involved in devising such circuits.

Perhaps the simplest way to envisage a coating is as an insulator separating the metal from the electrolyte. Such a sandwich of an insulator, or dielectric, between two conducting phases is by definition a capacitor. Accordingly, a suitable model comprises a capacitor C in series with the resistance R of the electrolyte and connections (Fig. 2 (a)). Indeed Nyquist plots corresponding to this are usually obtained for non-porous films immediately upon immersion. It then becomes interesting to examine the way in which the capacitance changes with time. By convention, it is often the practice to quote relative permittivity E_r values rather than capacitances:

$$E_r = \frac{Cd}{AE_0} \quad (13)$$

where d is the film thickness
 A is the specimen area
 E_0 is the permittivity of free space.

Fig. 4 shows the variation of E_r for a 2-coat vinyl lacquer (d.f.t. $120\mu\text{m}$) on polished steel. The measurements were made using the 2-electrode system described above and with the test cell (30cm^2) fixed to the panel. The initial capacitance was measured by filling the cell with mercury. The mercury was then removed and the test electrolyte (0.1M KCl) added and the capacitance determined at intervals. The plot of E_r versus time shows two distinct regions. There is a rapid rise during the first day followed by a much more gradual increase.

The E_r values for polymers are typically in the region of 2-10 whereas that for water is about 80. Thus the increase in the value of E_r with time can be explained by the absorption of water by the film. Furthermore, the fact that the curve shows two regions implies that there are two distinct mechanisms for water entry. A reasonable explanation is that, in the early stages water enters rapidly into capillaries or pores present on the surface of the film. These pores soon become saturated and thereafter the ingress of water is via the slower process of absorption by the bulk polymer. Thus a comparatively simple measurement, and model, yields considerable information on the structure and performance of the film.

Because paint films are imperfect dielectrics there is a variation of E_r with frequency and it is important to quote the frequency used for the measurement. E_r also varies with temperature and the technique of thermal dielectric spectroscopy TDS utilizes this fact. For example, Standish and Leidheiser used TDS to determine the glass transition temperature T_g of an epoxy film. They noted that exposure to water, for as little as a day, lowered the T_g considerably. This plasticisation of the film, it was argued, had profound implications with regard to its anti-corrosive performance since it would enhance the permeation of aggressive species.

Once electrolyte penetrates the coating, be it by any combination of pores or bulk diffusion, and accumulates at the steel surface, corrosion becomes thermodynamically inevitable. It is then encumbant upon the film to maintain the rate of corrosion at an acceptable minimum. It is clearly of interest to examine the ability of a.c. impedance to determine the success, or otherwise, of this corrosion control.

For aqueous corrosion to occur, electrical charge must be transferred across the metal electrolyte boundary. In other words, corrosion is an electrode process and, as such, is amenable to investigation by electrochemical polarisation. For unpainted

metals this is relatively straightforward and d.c. experiments can be used to measure corrosion rates. In the well-tried Stern-Geary method, for example, the specimen is polarised slightly (10 to 20 mV) from its rest potential and the current flow noted. This exercise yields a parameter known as the linear polarisation resistance R_p . Providing a number of assumptions hold R_p possesses the important property of indicating the rate of corrosion:

$$R_p \propto \frac{1}{i_{\text{corr}}} \quad (14)$$

where i_{corr} is the corrosion current.

It is presumed, therefore, that at the interface between a metal and a wetted coating there exists an analogous resistance to charge transfer R_θ which embodies information on the rate of underfilm corrosion. The paint technologist is therefore concerned with assessing R_θ . Regrettably, however, a simple d.c. measurement of the type outlined above is not suitable since the film imposes a high resistance in series with R_θ . On the other hand A.C. methods offer a prospect of determining R_θ in some instances. In order to examine how this is so it is useful to examine at first the a.c. impedance of an uncoated corroding metal. For this purpose a suitable equivalent model circuit has already been proposed by Randles (Fig. 5a) and a review recently published⁷.

Not only is charge transferred across a metal-electrolyte interface when corrosion takes place but there also exists some degree of charge separation. This constitutes a double layer capacitance C_d which couples in parallel with R_θ . Fig. 5a also shows a component W which is known as the Warburg impedance. This term is added to account for the fact that, even for bare metals, corrosion rates are influenced by diffusion processes. The electrochemistry enthusiast may be interested in the way in which W is derived from Fick's laws of diffusion. For the purpose of this work it is sufficient to note that, within certain frequency limits, W may be described:

$$W = \frac{\sigma}{\sqrt{\omega}} - \frac{j\sigma}{\sqrt{\omega}} \quad (15)$$

Where σ is the Warburg coefficient.

It has equal real and imaginary components and hence forms a 45° slope with the real axis in a Nyquist plot. Since the diffusion of ionic species is a comparatively sluggish process, it is unperturbed by high frequency signals. However, as the frequency becomes reduced the contribution of diffusion phenomena to the total impedance increases. Ultimately, however, the line curves back to the real axis.

Randles' circuit also contains a resistance R in series with the electrochemical components. This embodies the purely ohmic resistances of the electrolyte and connections. It displaces the electrochemical part of the Nyquist plot along the real axis. Figs 5 (b)-(d) are schematic Nyquist plots, based on Randles' circuit, which show the corrosion rate controlled (a) solely by the energy barrier to charge transfer, R_θ (b) a mixture of R_θ and diffusion processes W and (c) W alone. Experimental curves of all three types are to be found in the corrosion literature.

One approach to studying corrosion of coated metals is to modify Randles' circuit to take account of the impedance contribution of the film. The question naturally arises as to how R_θ , C_d and W should be coupled with the film impedance. The answer to this depends upon the structure of the metal-coating-electrolyte system; or more correctly upon the experimenter's perception of that structure! Two limiting cases may be envisaged. In the first, or porous film, model corrosion occurs exclusively at the bases of pores which penetrate to the metal

surface. In the second, continuous film, model corrosion is taken to occur under a continuous, defect-free coating.

Porous Films

Fig 6 (a) shows the model circuit proposed by Beaunier *et al*¹⁰ for a film containing one or more pores penetrating through to the metal surface. The film capacitance C_f is in parallel with a series combination of the electrolyte in the pore R_e and the impedance of the corrosion reactions Z_c at the base of pores.

The applicability of this model was illustrated by creating an artificial pore in an otherwise intact film. Fig. 7 shows the Nyquist plot for a vinyl lacquer film (120 μm) on polished steel. Before creating the defect the response was almost purely capacitive, which confirms its continuous nature. A small pin prick was then made in the coating and the impedance curve determined after 6 hours. The result is a high frequency parallel R-C type semi-circle and a low frequency Warburg type response. Analysis of the semi-circle using the relationships in equations (9)-(11) shows that the capacitance is that associated with the intact paint film and the value of R is consistent with the known conductivity of the electrolyte and reasonable estimates of the dimensions of the pore. It should not be surprising that the electrochemical impedance shows diffusion control considering the tortuous path along which reacting species must be transported.

Fig. 7 also shows the impedance curve obtained after 4 days immersion. The diameter of the semi-circle has become larger indicating that R_e has increased. This is consistent with the pore becoming partially blocked with corrosion products. The capacitance associated with this semi-circle has increased slightly from 28 to 30 pF/cm² which is consistent with the bulk film having continued to absorb water.

Similar impedance curves were obtained for a thin (20 μm) cathodic electropaint lacquer applied to phosphated steel (Fig. 8). Although this film did not contain a gross defect of the type inflicted upon the vinyl panel, a curing agent catalyst was deliberately omitted from the formulation. This resulted in the film failing to achieve full cure even after the subsequent stoving treatment. The impedance curve obtained soon after immersion was essentially capacitive but within a day a notable real component had developed. After 60 days the curve had developed into a shape similar in form to that of the punctured vinyl. There is a high frequency semi-circle associated with the film and a lower frequency curve deriving from the electrochemical reactions.

It seems reasonable to interpret this behaviour in terms of a pore model also. Instead of the crude pore made in the vinyl the R_e value in this latter case is presumably associated with the progress of water via regions of low cross-link density. In the corresponding experiment in which the curing catalyst was included, only capacitive type behaviour was observed throughout the test. Inspection of the panels at the end of the immersion period (60 days) showed no breakdown of the fully cured specimen whereas the part-cured film showed both blistering and underfilm corrosion. In this case at least it seems that the development of a real component of the impedance within a single day is associated with the subsequently observed failure. This illustrates the usefulness of a.c. impedance as a predictor of coating failure.

The porous film model, therefore, seems well suited to some metal-coating-electrolyte systems. Mansfeld *et al*¹¹ have used it to rank the effectiveness of various steel pretreatments in relation to the corrosion protection afforded by polybutadiene. Similarly the occurrence of Warburg type behaviour for steel coated with vinyl-acrylic films has been taken to indicate corrosion at the base of pores¹². In general it is to be supposed that the thinner the coating

is the greater the likelihood that pores will penetrate to the metal surface. A corollary is that thicker, multicoat, systems are less amenable to analysis in the same manner.

Continuous Films

Fig. 6(b) shows a circuit describing corrosion under a "defect-free" coating. In this case the parallel capacitance C_f and resistance R_f of the wetted films are coupled in series with the electrochemical type components of the Randles type circuit. Walter¹³ has used the model shown to explain impedance curves for vinyl covered aluminium and galvanised steel coated with a silicone polyester; both of which were immersed in 5% NaCl. He found that computer synthesised curves, using suitable component values, gave reasonable agreement with the measured data. Nevertheless, despite this and other work using related continuous film models, the recent trend has been to adopt a porous film model for impedance curves exhibiting features associated with corrosion reactions. Indeed, in a more recent publication³, Walter himself has opted for a porous model.

That ambiguity should exist between the two models is not really surprising. It has already been pointed out that the art of fitting circuits to measured impedance data is by no means precise. In fact it is possible, by suitably manipulating component values to explain a given curve by either of the two models. It should further be borne in mind that these models only represent the limiting cases in a continuum of situations. It is not hard to conceive that by progressively reducing the diameters, and increasing the numbers, of "pores", then a "continuous" film is arrived at wherein electrolyte is transported by bulk diffusion.

As was shown above, the impedance response of an intact barrier type film (120 μ m vinyl) during the early stages of immersion is mainly capacitive. Similar behaviour is also reported in the literature for freshly immersed moderately thick, carefully prepared films of chlorinated rubber and coal tar epoxy on steel¹⁵ and polyurethane varnish on iron¹⁴. As the immersion continued, however, a real component of the impedance was reported in all cases to develop giving rise eventually to parallel R-C type semi-circles for which the value of R continued to decrease with time. Both sets of workers were, therefore, keen to ascribe a meaning to the parallel resistive component; the capacitance being compatible with the wetted films.

Piess and Verbist¹⁴, studying the polyurethane varnish on iron, concluded that the resistance represented the ionic resistance of the coating which decreased as it took up water. Although they could observe underfilm corrosion developing, they were not able to elicit an electrochemical type of response from their specimen. They, therefore, concluded that, in the case of intact, high resistance films, the impedance of the underfilm corrosion processes is completely masked by that of the film.

The experimental observations of Scantlebury *et al*¹⁵ for the clear chlorinated rubber lacquer were essentially similar. These latter workers were, however, less inclined to dismiss the technique. Without specifically attributing the value of the parallel resistance to a single parameter of the metal-coating-electrolyte system they did regard it as significant. Since the underfilm corrosion spots did not appear until R had developed and, further, since the corrosion proceeded as the magnitude of R reduced they contended that it "is related to corrosion processes under the film, and a knowledge of the former (R) could be a useful indication of the latter."

Summary

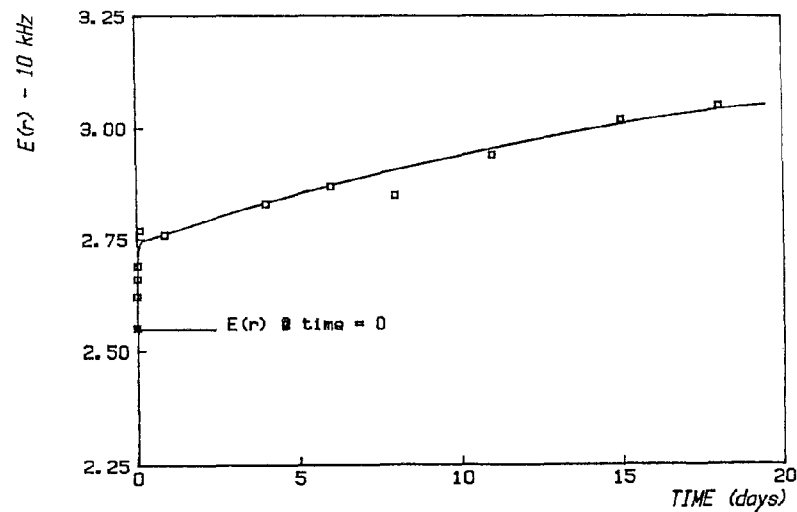
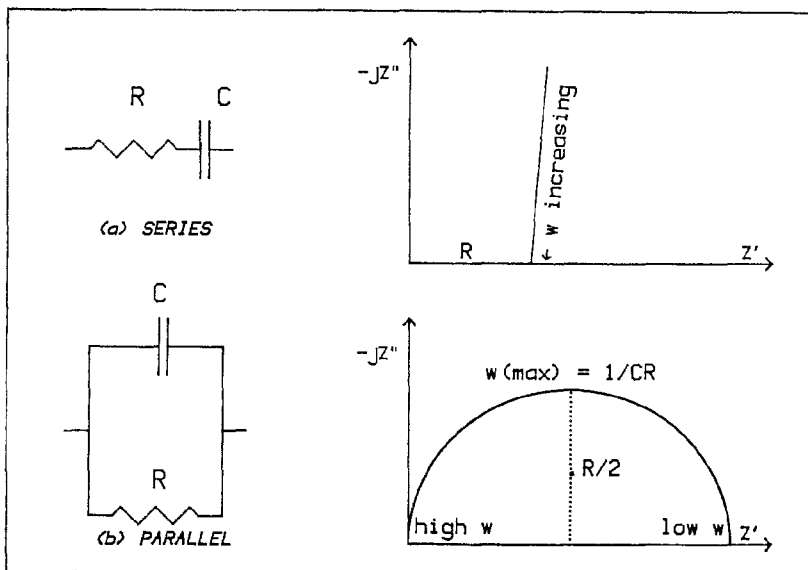
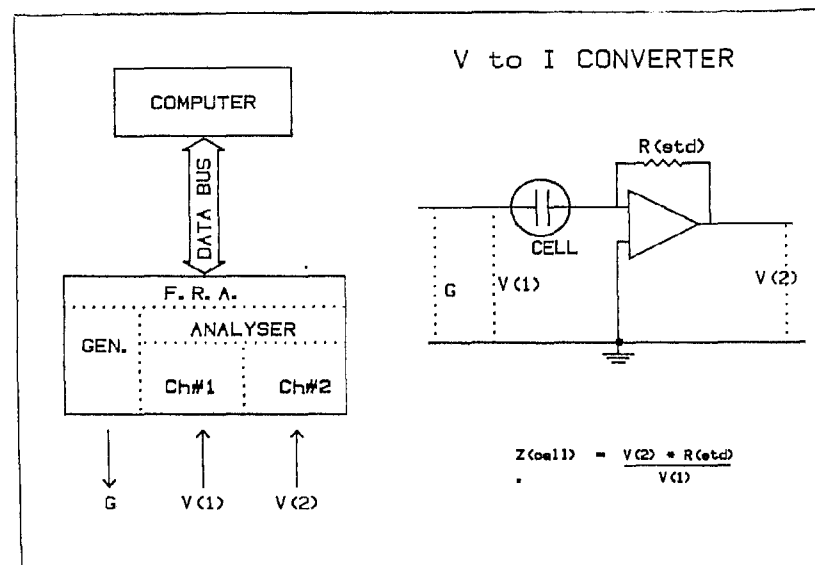
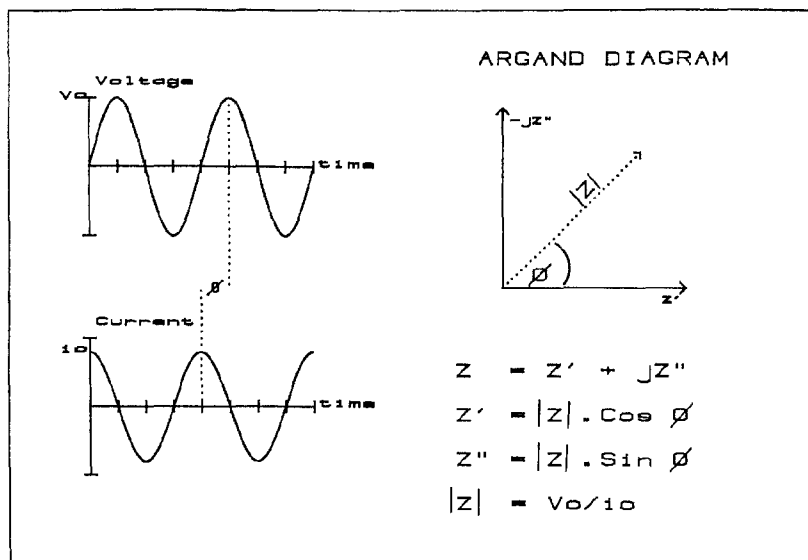
A.C. impedance data can be obtained for immersed coated metals using a frequency response analyser and suitable interface. The value of the data obtained in assessing the anticorrosive performance of the coating depends on the selection of a suitable equivalent circuit to model the system. In the case of thin or porous films, the impedances of the corrosion processes are accessible and may be interpreted by assuming a parallel coupling with the film impedance. For thicker, barrier type coatings, however, the impedance of corrosion processes at the metal-wetted coating interface will be screened by that of the coating. In these latter cases the value of a.c. impedance is believed to lie in its ability to monitor changes in the film's property which, in turn, relate to its protective capability.

Acknowledgments

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References

1. Scantlebury, J. D. & Ho, K. N., *J.O.C.C.A.* 62 (1979) 9.
2. Callow, L. M. & Scantlebury, J. D., *J.O.C.C.A.* 64 (1981) 83.
3. Walter, G. W., *J. Electroanal. Chem.* 118 (1981) 259.
4. Standish, J. V. & Leidheiser, H. J. *Coatings Technol.* 53 (1981) 53.
5. Stern, M. & Geary, A. L., *J. Electrochem. Soc.* 104 (1957) 56.
6. Randles, J. E. B., *Disc. Faraday Soc.* 1 (1947) 11.
7. Hladky, K., Callow, L. M. & Dawson, J. L., *Br. Corros. J.* 15 (1980) 20.
8. Szauer T., *Prog. Org. Coatings* 10 (1982) 171.
9. Sluyters-Rehbach, M., & Sluyters J. H., in "Electroanalytical Chemistry" ed A. J. Bard, Dekker N. Y. 4 (1970) pp16-17.
10. Beaunier, L., Epelboin, I., Lestrade, J. C. & Takenouti H. *Surface Technol.* 4 (1976) 237.
11. Mansfeld, F., Kendig, M., Tsai, S., *Proc. Int. Congr. Met. Corros.* /8th Mainz 1981.
12. Callow, L. M., & Scantlebury, J. D., *J.O.C.C.A.* 64 (1981) 140.
13. Walter, G. W., *Conf. Australan. Corros. Assoc.* (1977) paper K2.
14. Piess M. & Verbist, R., *FATIPAC* (1980) 163.
15. Scantlebury, J. D., Ho, K. N., & Eden, D. A., "ASTM-Progress in Electrochemical Corrosion Testing" (1980) 187.



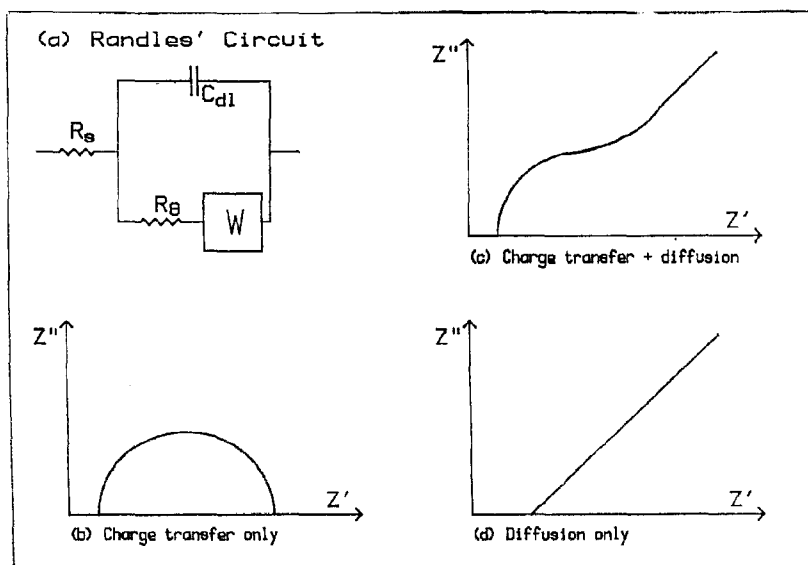


Fig 5 MODEL CIRCUIT FOR UNCOATED ELECTRODE

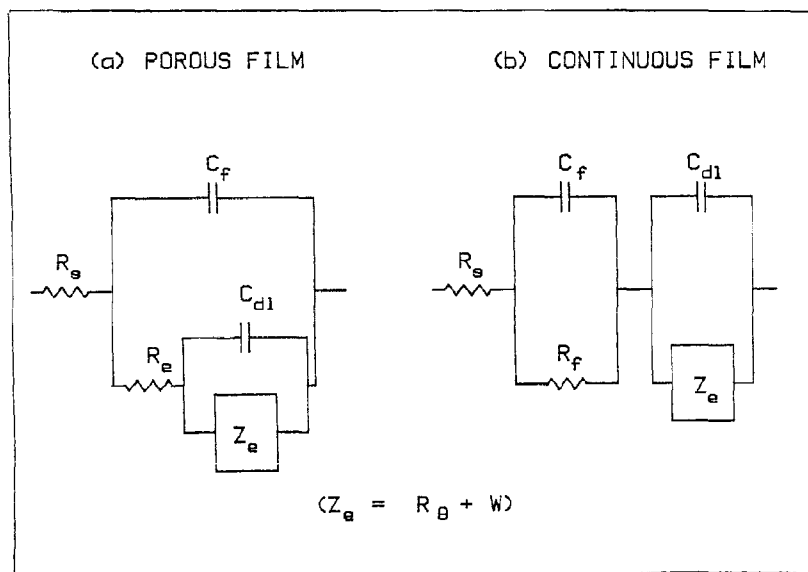


FIG 6 MODEL CIRCUITS FOR COATED ELECTRODES

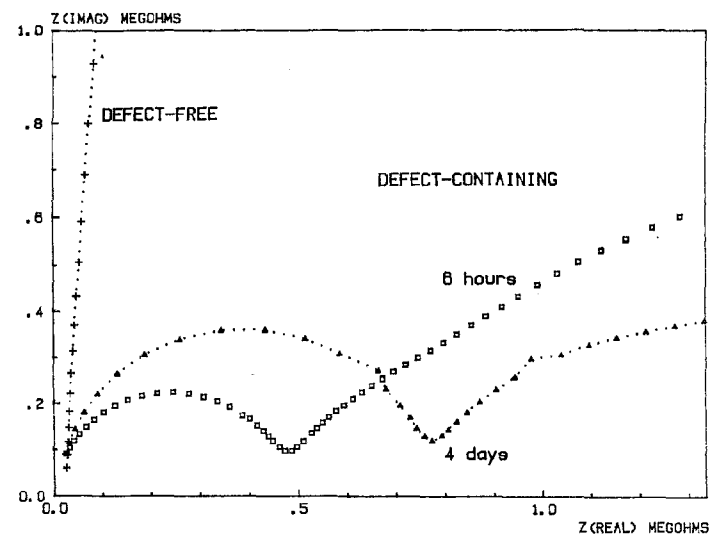


Fig 7 VINYL FILM (WITH DEFECT)

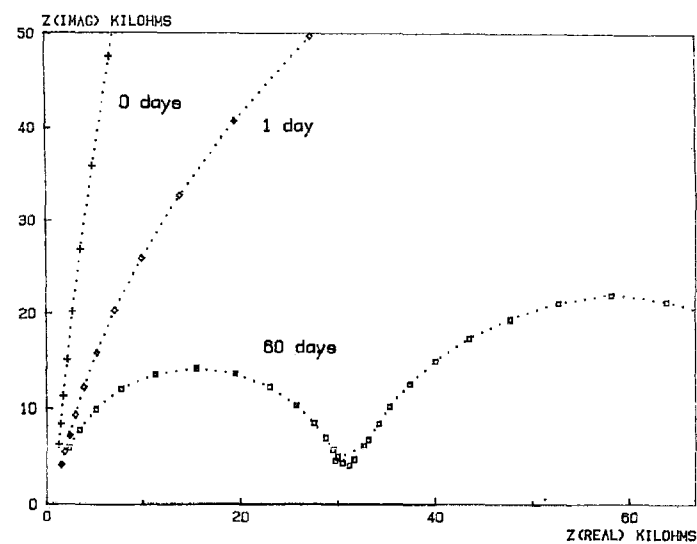


Fig 8 ELECTROCOAT (A) IN SEA WATER