Manufacturers Roundtable

# Regional Player Perspective

The paint and coatings industry faces several critical issues today. Consolidation, rising raw material and energy prices, and increasingly stringent regulatory requirements impact the daily activities of suppliers and manufacturers. Overall the goal remains to provide high performance paints and coatings at an affordable cost—in essence to meet the needs of the end user, whether a consumer or professional painting contractor. Remaining competitive with the large national paint and coatings manufacturers has become a significant challenge for smaller regional producers over the past several years. The growing regulatory pressures have become the primary concern of these players in the paint and coatings marketplace. Working closely with regulators on the one hand and customers on the other, as well as investing in innovative technologies, will be the keys to success, according to the companies participating in this roundtable discussion. JCT CoatingsTech spoke with Anthony M. Ciepiel, president of The Flood Company; Jim Capitano, vice president of manufacturing with Duron, Inc.; and Tim Bosveld, vice president of marketing for Dunn Edwards.

**JCT:** *What would you identify as the top three most critical issues facing the paint and coatings industry over the next five years? Why do you classify them as critical, and what impact will they have on the industry?*

*Anthony M. Ciepiel, Flood:* The number one issue facing the industry is the need to create low-VOC (volatile organic compound) paints and coatings that do not compromise performance and can be economically produced. It is easy to create low-VOC formulations, but not easy to do so and maintain the level of performance demanded by the customer. It is yet another challenge to do so at an economic price.

*Jim Capitano, Duron:* For companies that operate in different geo-

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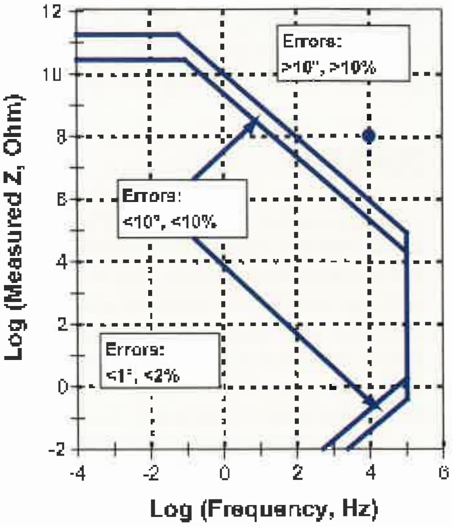


Figure 8—This Bode plot shows the likely errors in the measured impedance for a given frequency for a commercial potentiostat.

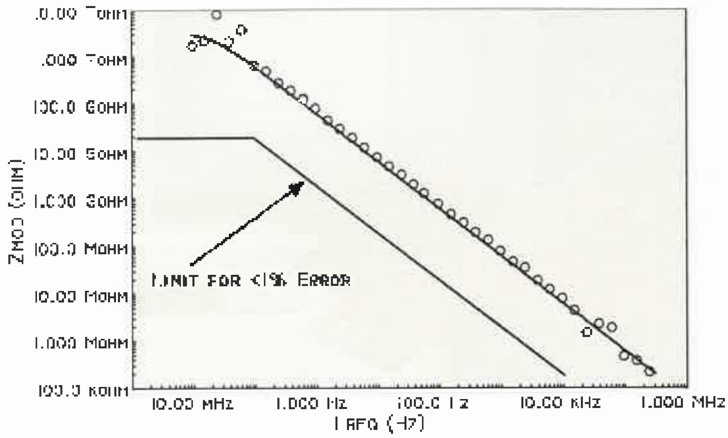


Figure 9—The "Open Lead" curve for a commercial potentiostat. Also shown is the manufacturer's estimation of the highest impedance that can be measured with a 1% error or less.

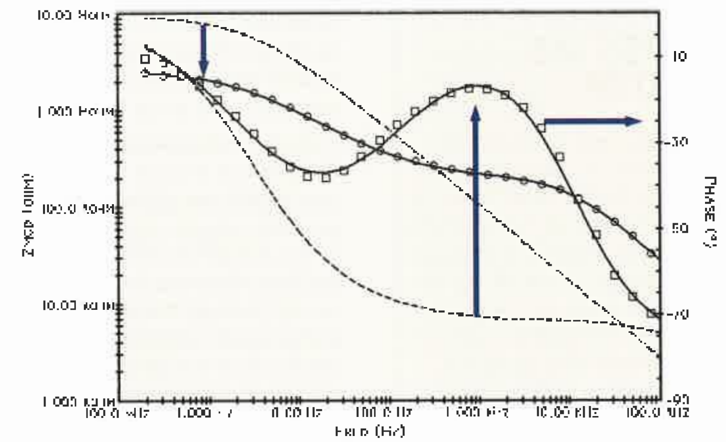


Figure 10—A fit to a more complicated model. The curve for the initial estimates for the parameters is also shown.

the whole frequency range. This gives the high frequency data an equal weight with low frequency data.

Making EIS measurements at very high or at very low impedances, or at very high frequencies, is a difficult task. At any of these extremes you may be able to make the measurement, but it may not be a meaningful or useful one. At both very high impedances and at very low impedances, you may be measuring the characteristics of your cell geometry, or of the wiring, or of your potentiostat, and not the characteristics of your coating or corrosion reaction. Many, but not all, potentiostat manufacturers will specify the impedance and frequency limits for making reliable and accurate measurements that reflect the sample you are trying to study. It is important to be aware of the limits. *Figure* 8 shows how the errors in the impedance depend on the frequency and on the impedance. For example, consider measuring a sample with a $10^8$ ohm impedance at 10 kHz ($10^4$ Hz). Although the measurement may be possible with this potentiostat, *Figure* 8 indicates that the errors will be greater than 10°/10%. The errors will be significantly greater since the impedance/frequency point is far from the dividing line.

## OPEN LEAD CURVE

Fortunately, there is quick and simple way to test the sensitivity of an EIS system. To determine the maximum impedance that can be measured with a particular EIS instrument, run an EIS curve with no cell attached to the instrument. The reference and counter electrode leads must be connected together. If a "sense," "working sense," or "RE2" lead is provided on your potentiostat, it must be connected to the working electrode lead. All of the cell leads should be placed in a grounded Faraday Cage. Impedances higher than the Open Lead impedance cannot be measured. The Open Lead Curve of a commercial potentiostat is shown in *Figure* 9. The impedance at 10 kHz is about 10 Mohm ($10^7$ohm). Therefore, at 10 kHz, the highest sample impedance that can be measured with this instrument is $10^7$ ohm. However, there will be substantial error in the measurement. At 0.1 Hz, this instrument can measure, at most, $10^{12}$ ohm. To be sure that the measured impedance has less than a few percent error in the magnitude, or less than a few degrees error in phase, the impedance must be 50 to 100 times lower than the limits estimated from this "Open Lead" experiment. At 0.1 Hz, then, the maximum impedance that can be measured with acceptable accuracy is $10^{10}$–$10^{11}$ ohm.

A similar estimation of the limits of error at low impedances can also be made. In this case, all of the potentiostat leads are nominally shorted together. This is not as easy an experiment to do. Fortunately, sub-ohm imped-


*A computerized electrochemistry instrument with an Electrochemical Impedance Spectroscopy plot. The actual electrochemical instrument is draped over the keyboard.*

ances will not be encountered in the coatings laboratory, and details of that experiment will not be covered here.

## DATA ANALYSIS AND INTERPRETATION

Once data has been collected, the next step is to analyze the results. Several methods can be used. Some of these will be described in Part 2 of this series. Some of the analysis techniques rely upon the measurement of the impedance or phase angle at a single frequency. These can be used in a QC or QA setting, but only after there is a deeper understanding of the actual mode of coating degradation or failure.

It is tempting to say that you should explain your impedance data based upon a physio-chemical model derived from first principles. Although this makes an excellent treatise, few of us have the luxury of time to complete this task.

A more commonly applied approach is to create an equivalent circuit model. This approach makes the analogy between the processes in the electrochemical cell and electrical circuit components such as resistors and capacitors. This is a very useful technique, but must be applied with some caution. It is not sufficient to create a model that fits your EIS data without also showing the relationship between the circuit elements you have used in your circuit model, and physical or chemical-processes that occur in your coating.

Most of the models begin with Randles cell that we have discussed. A nonlinear least squares technique is generally used to determine the values of the circuit elements (resistors and capacitors) that best fit the EIS data taken on the coating. Because the mathematics becomes complicated when even two or three circuit elements are used, the optimum values generally cannot be computed analytically or in closed form. An iterative approach is used. It begins with a rough estimate for the circuit element parameters and then refines that guess until the best fit is obtained (see *Figure 10*). Fitting programs are available from several sources. Nearly all require that the user select a suitable model and provide the first guess of the circuit parameter values. A library of models is generally available, along with the capability of designing your own model. The resistor and capacitor discussed in this article are only the tip of the iceberg. Many other special purpose circuit elements have been invented by the electrochemist to model other processes. Examples are diffusion (the Warburgi impedance), or a chemical reaction that precedes the electron transfer (the Gerischer impedance).

## SUMMARY

EIS is a general purpose electrochemical technique applicable to virtually all areas of electrochemistry. In this article, we have covered the basics of electrochemical impedance spectroscopy: the theory behind the measurements, the equipment and cells required for painted samples, how to use them, and an introduction to equivalent circuit modeling of the collected data.

The next article in the series will focus on the physical description of a coating on a metal surface, how that relates to circuit elements for data fitting, the experimental pitfalls, and, finally, analysis of the different stages of coatings degradation. In the final article, we will discuss how coatings scientists use the various methods available to get an understanding of failures modes of coatings.

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