The paint and coatings industry faces several critical issues today. Consolidation, rising raw material and energy prices, and increasing 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 Bosweld, 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 geographical areas, the inconsistency in air quality regulations from region to region poses a significant challenge. It appears that many of the regulations are established as part of a political process rather than through scientific exercise and therefore often are not based on sound science.

The spiral of increasing raw material costs also poses a challenge today. It is difficult to pass these rising costs through to customers, and therefore profit margins are being eroded. The paint and coatings market is very competitive today, and there is always someone willing to take market share by lowering prices and profits. We see in the middle and are being squeezed by basic commodity suppliers on one hand and large customers on the other. This scenario is driving consolidation, which will only continue into the future.

Difficult in recruiting new talent is a third major issue for Duron. There is a perception that the paint industry is stodgy and therefore is not exciting or attractive to new talent.

Tim Bosweld, Dunn Edwards: In addition to the increasing VOC regulations, we are facing escalating raw materials prices and the costs to defend against class action suits related to construction defects. Some of the factors driving up raw materials prices are unprecedented Chinese economic expansion and higher oil prices. In the case of class action suits, lawyers have the ability to bring on these suits, such as mold and mildew, whether they are valid or not. We find ourselves spending more on consumer education and legal expenses to combat this trend.

JCT: What can individual companies and/or the industry as a whole do to manage these issues?

Anthony M. Ciepiel, Flood: We as individual companies and as an industry must work together with regulators to develop reasonable guidelines and timetables for implementing more stringent VOC requirements.

Tim Bosweld, Dunn Edwards: Education of regulators is also very important. There are sustainability and eco-efficiency issues that need to be addressed. One consequence of reduced performance of paints and coatings will be more frequent painting, which in turn will result in increased raw material consumption and waste generation. There is a balance between lack of performance and VOC limits that needs to be considered.

Companies must also develop better mechanisms for product development and find more efficient ways to get products commercialized at a much faster rate. We need a much faster pace of R&D to achieve technological innovations that will enable low VOC formulations to have performance with affordability. Education is also critical for addressing the construction defects issue. They also need to be informed about how to prevent their formation.

Jim Capitano, Duron: Consolidation on both the raw material supplier side and paint manufacturing side will continue. In order to prevent further margin erosion, companies need to work closely with both suppliers and customers to continually develop products that provide the performance properties valued by the customer. Making sure that customers understand the value that is provided is also important and may enable paint producers to pass on some of the rising raw material and energy costs.

In order to attract talent, the industry will be beneficial from a public relations effort. The paint and coatings industry is a strong industry and continues to grow at a steady rate. It is one of the only industries with domestic manufacturing jobs available and has a lot to offer at all levels of employment. Not enough people are aware of these facts.

JCT: Where do the opportunities lie for the paint and coatings industry, and how is your company planning to take advantage of them?

Jim Capitano, Duron: The greatest potential is where paint and coatings manufacturers can develop strong relationships with their customers. Focusing on meeting their needs and providing them value with high performance products and a solutions approach will lead to opportunities for growth.

Tim Bosweld, Dunn Edwards: The Internet has tremendous potential to improve the efficiency of most aspects of operations in the paint and coatings industry.

The Internet has tremendous potential to improve the efficiency of most aspects of operations in the paint and coatings industry.
ACQUIRING THE DATA: CELL AND INSTRUMENTATION

Figure 6 shows a typical cell for making impedance measurements. The cell is constructed in the same manner used in everyday electrochemical measurements, such as for studying corrosion. A sample electrode (working electrode), a reference electrode, and a counter electrode are immersed in an electrolyte solution (for instance, 5% NaCl in water). The reference electrode is typically a saturated calomel electrode (SCE) and the counter electrode is usually an inert material like a platinum mesh or a carbon rod. There may be a provision for stirring and for removing oxygen from the electrolyte.

The instrumentation (Figure 7) required includes a waveform generator to produce the sine waves and potentiostat to control the potential. It must control both the dc current as well as the added ac excitation voltage. The instrumentation must also contain a means of accurately measuring the ac components of both the voltage and the current and the phase relationship between them. This data is used to calculate the impedance of the cell. Because of the complexity of optimizing and coordinating these ac measurements, a computer is generally used to run the experiment and to display the results in real time.

Figure 7—A block diagram of the modern instrumentation used to make the EIS measurement. Often, more than one of these functional blocks are included in a single instrument, or even inside the computer.

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 estimate 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 estimate for the parameters is also shown.

Over the years, various techniques have been used to measure the current and voltage amplitudes and the phase relationship between them. Early measurements were done manually using an oscilloscope or an impedance bridge. Today, the measurements are computerized and the ac components may be measured with a frequency response analyzer, with a lock-in amplifier, by using Sub-Harmonic Sampling, or by using a Fourier transform technique. All of these methods are capable of measuring the impedance with suitable accuracy. In a practical sense, more errors may be introduced by the potentiostat.

The data collected by the computer program should include the frequency of the ac waveform and either the magnitude and phase of the impedance at each frequency, or the real and imaginary components of the impedance, or perhaps both. Most modern programs allow the display of either or both of these equivalent display formats, the Bode plot or the Nyquist plot. Other parameters, such as the dc current and dc voltage are often recorded as well, and can be useful in interpreting the data in some of the more complicated systems. This additional information is often needed, however.

A small (5–10 mV) amplitude ac signal is applied to the sample by the potentiostat and the current response is analyzed to extract the phase and amplitude relationship between the current and the voltage signals. In some applications, larger signals can be applied, but care must be taken to ensure that the system is linear over the ac voltage range. In studying base metal corrosion, larger amplitudes are almost never used.

The data is transferred to the potentiostat and the Bode that references the working electrode (Figure 7), only the impedance between these two electrodes is measured. The impedance at the counter electrode and the resistance through the bulk of the solution is not sensed when a three-electrode potentiostat is used.

The number of cycles used to collect the data determines the precision of the measurement. At low frequencies, the trade-off between the length of the experiment and precision is a serious consideration. A single cycle of a 1 kHz sine wave takes 1 min. Although sampling many cycles would improve the precision of the measurements, to do so would lengthen the experiment and increase the chances that the sample changes during the experiment. The theory of EIS requires that the system be stable and unchanging as well as linear. Unfortunately, for some extremely impervious, high impedance coatings, data must be taken at low frequencies, sometimes even lower than 0.001 Hz. To be fair, however, even a slow, 0.001 Hz (27 h per cycle) experiment which will take days to complete is faster than waiting months or years for an exposure test to be completed.

The impedance is usually measured as a function of frequency over many decades, for example from 100 kHz to 1 kHz. For this reason the measurement points are chosen logarithmically to get an even spread of points across the whole frequency range. This gives the high frequency data an equal weight with low frequency data.

Making EIS measurements at very high or very low frequencies, or at very high frequencies, is a difficult task. At any of these extremes you may be able to make the measurements, 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. Still, but 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 these impedances depend on the frequency and on the impedance. For example, consider measuring a sample with a 10 ohm impedance at 10 kHz (10^9 Hz). Although the measurement may be possible with this potentiostat, Figure 8 indicates that the errors will be significantly greater than 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 "RED" 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 (10^9 ohms). Therefore, at 10 kHz, the highest sample impedance that can be measured with this instrument is 10^9 ohm. However, there will be substantial error in the measurement. At 0.1 Hz, the instrument can measure at most, 10^2 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 at least 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 ohm. A similar estimate 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 experiments to do. Fortunately, sub-ohm impedances...
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 fo- cus on the physical description of a coating on a metal substrate, how resistors and capacitors relate to the elements for data fitting, the experimental pitfalls, and, finally, an analysis of the different stages of coating degradation. In the final article, we will discuss how coatings scientists use the various methods available to get an understanding of failures of coatings modes.

BIBLIOGRAPHY


