Developments in Ternary Electroless Nickel Deposits

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Electroless nickel processes have been the basis for a range of innovative coatings since their inception in the 1950s.[1] This paper will discuss a new ternary alloy process, its properties and how these properties have been used to create new markets for the product. Properties discussed include corrosion resistance, hardness, wear resistance and ductility and also the effect of temperature on the deposit.

Keywords: *Electroless nickel, ternary alloy, electroless alloy plating*

Introduction

Electroless nickel deposits have been used for decades with considerable success and have seen large growth due to the unique properties offered by the codeposition of a nickel-phosphorus or nickel-boron alloy. Many of these properties, which include offering hardness, corrosion resistance and uniform deposit thicknesses, can also be altered by the adjustment in phosphorus or boron concentrations, giving a flexibility which is extremely unusual. Applications where electroless nickel has found a strong market include computer hard drives, telecommunication systems, oil extraction equipment, aerospace connectors, automotive transmission and fuel systems.[2]

Since the deposits started to be used commercially in the 1950s,[3] there has also been considerable interest in making further improvements to the deposit performance by the introduction of other metals or particles into the alloy.[4]

The incorporation of particles is now well established with composites containing PTFE, diamonds, boron nitride and silicon carbide all being commonly used in the market.[5] However, the use of ternary and tertiary alloys has not been as successful. The normal reason for incorporating another metal into the deposit would be to improve the performance of the coating, by providing increased hardness or wear resistance, or to improve the corrosion resistance.[6] Their use to improve their solderability has also been reported.[7]

An incomplete list of the metals which have been added to electroless nickel to improve the deposit includes: copper, iron, tungsten, cobalt, rhenium, molybdenum and tin. Some of these have been moderately successful commercially, but none have reached a position where the advantages in performance outweigh the expense and operational difficulties in using the chemistry sufficiently to make the process well established. One process did find a limited market. This was a deposit containing about 1% copper, with claims of much improved corrosion resistance,[8] but this chemistry is no longer widely used.

The requirement for a deposit that offers more than the now standard process still exists and demand for improved performance, at a similar or lower cost, is increasing even in these difficult times. This paper looks at one such ternary alloy and the advantages it offers as well as some of the potential difficulties found in its use.

Ternary alloy testing

The ternary alloy tested was a nickel-phosphorus-tin alloy, produced from an acid electroless nickel solution. The reason for the choice of this alloy was that there had been references in literature[9] that indicated that the use of nickel phosphorus with a tin topcoat potentially offered much improved corrosion resistance over a standard high phosphorus electroless nickel. Further, the basics of a chemistry to do this were already available.

The chemistry operates conventionally using a pH of 4.6 and a temperature of 86 to 90°C. All testing was carried out either using a 2.0-L beaker run on a thermostatically controlled hot plate, or in a 75-L polypropylene plating tank, heated using PTFE coated electrical heaters and filtered continuously through a 1-μm cartridge filter at a rate of five solution volumes per hour.

The amount of tin which can be added to the bath is limited. Although there are claims for a tin content in the deposit of as high as 8 wt%,[10] our experience suggested that to achieve this would require such a high concentration of tin in the solution that the

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plating rate would fall to unacceptable levels and the bath would become over-stable. This type of chemistry would not be commercially viable.

The following tests were carried out: hardness, wear (Taber testing), NSS, CASS, electrochemical corrosion rates, temperature of crystallization, magnetic sensibility, as well as alloy content and alloy distribution. Also studied was practical data such as plating speed and operational stability when running the plating solution.

Corrosion testing was normally carried out using steel panels, although some work was also carried out on aluminum panels and actual customer components.

The testing continued until 24 g/L of nickel had been deposited from the plating solution, equivalent to four MTOs (metal turnovers) of a conventional 6 g/L plating bath.

Test results

Speed

The plating speed obtained from the solution is slower than a conventional high phosphorus bath, but is very consistent throughout the solution life (Fig. 1). This speed can be increased (in the same way as when plating in conventional solutions) by the use of a higher temperature or pH. However, if the speed is increased too much, the quality of the alloy deposit is compromised. After four MTOs, the speed starts to fall and the operation of the bath is no longer recommended.

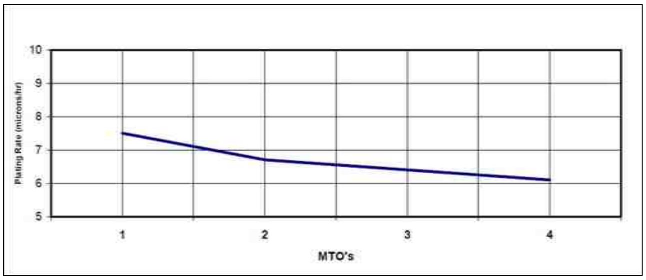


Figure 1—*Plating speed.*

Stability

It is extremely important to keep the solution strength between 90 - 100% activity. If the chemistry is maintained between these concentrations, experience has shown that the plating bath is extremely stable in both anodically protected stainless steel as well as polypropylene tanks. The stability was assessed by the time taken to start nickel plating on the basis of a beaker when testing in the laboratory using a hot plate with a magnetic stirrer bar. In this equipment the tendency to create roughness in the solution and the frequency of cleaning requirements for the customer's plating tank were the factors used. Although this is highly subjective, it was felt that sufficient experience existed within the R&D team to make this assessment valuable. Using this assessment, the bath was seen to be at least as stable as a conventional high phosphorus bath if it was controlled adequately. If the bath was not controlled correctly it showed a greater tendency to plate up than conventional processes.

Alloy content

The alloy content is extremely important. If the deposit contains too much tin, then it stops acting in a catalytic fashion and the electroless nickel plating will stop. Conversely, if the amount of tin in the deposit is too low, then there are limited advantages in plating an alloy deposit rather than a conventional high phosphorus (10 - 12 wt% phosphorus) deposit.

The tin tends to rise slightly as the bath ages, although this can be controlled by pH and temperature to speed the bath plating rate and reduce the amount of codeposited tin. Figure 2 shows the alloy from the bath as measured by the dissolution of the deposit and analysis by ICP. Generally the alloy should be within the range of 1 - 4 wt%, and this is reflected in the corrosion resistance offered by the deposit.

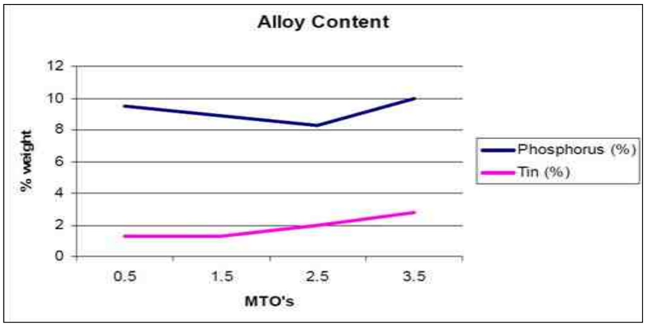


Figure 2—*Deposit alloy composition.*

Deposit stress

It is critical to ensure that the stress of an electroless nickel deposit remains slightly compressive or only moderately tensile. Otherwise, the deposit will show poor performance for both wear and corrosion resistance. The ternary alloy is initially slightly compressive (when measured using a spiral contractometer) but becomes more tensile as the bath ages, as is typical with high phosphorus electroless nickels. However, when compared to conventional high phosphorus systems, the stress remains low even after four MTOs (Fig. 3). In most conventional high phosphorus baths the stress becomes highly tensile between four and five MTOs and the bath therefore loses many of its positive properties in respect to corrosion resistance.[11]

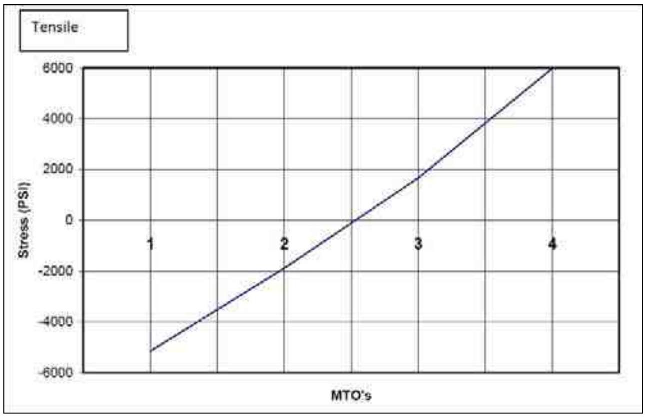


Figure 3—*Deposit stress.*

Corrosion resistance

There are two aspects to corrosion when specifying an electroless nickel deposit: the actual chemical resistance of the deposit and the barrier protection the deposit offers to the substrate. The corrosion resistance of the deposit has been measured using electrochemical dissolution as discussed in previous technical papers.[11] The alternative of studying the rate of dissolution in various mediums was perceived to be too slow for the requirements of this paper.

For corrosion protection, both CASS and NSS was used as these are industry standards and well known even though there may be limitations concerned with assessing the results. The main concern is the effect of porosity, as one small defect will cause failure in a way not usually seen in practice. The NSS testing took place on steel panels with a range of thicknesses. These results were compared internally with results found by independent customer testing on actual components and a good correlation was found, which confirmed the laboratory results as realistic. These results are shown in Fig 4.

The tests were stopped at 1920 hr, and showed that it was possible to get very good corrosion performance from a new solution, with just a 12.5-μm deposit, and 25 μm gave >1920 hr performance throughout the solution life. Results were also good when tested on aluminum, with 25 μm of deposit giving in excess of 2000 hr corrosion resistance, as shown in Fig. 5.

The electrochemical results (shown in Table 1) were interesting in that they indicated that in a chloride environment, the corrosion rate was only about 60% of a conventional high phosphorus deposit and that there is an optimum concentration of tin which is less than would be expected from the literature (Fig. 6).

Table 1

Electrochemical corrosion rates of various electroless coatings prepared from fresh baths (0 MTO) compared to an uncoated steel substrate

EN Process	Corrosion Rate (mpy)
10-12%P - Conv.	2.88
10-12%P - ELV	2.42
10-12%P - Alloy	1.56
Steel	16.79

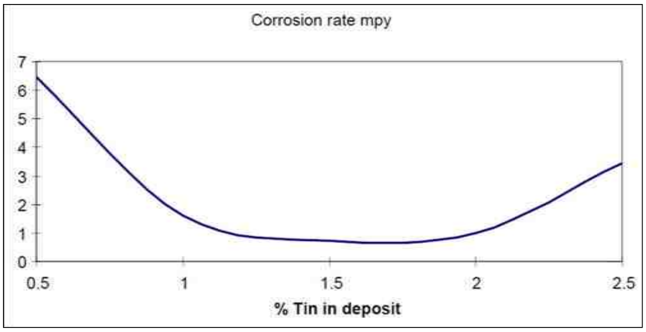


Figure 4—*Corrosion resistance.*

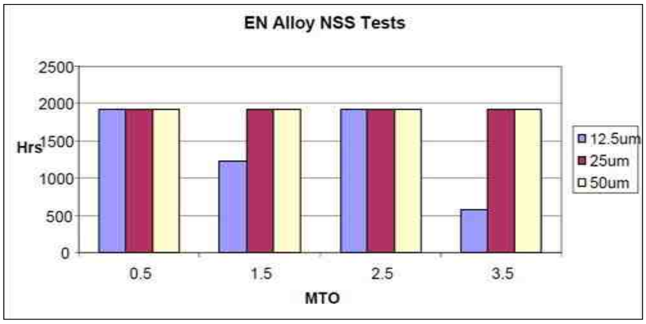


Figure 6—*NSS test results (Test stopped after 1920 hr, most panels still without red rust).*

The testing in CASS was not as differentiated as expected. Panels plated were compared to a RoHS-compliant lead-free high-phosphorus deposit, and no obvious difference was seen. The results for the ternary alloy deposit are shown in Fig. 7. The results gave about 100 hr for 12 μm, and 200 hr for 20 μm for both systems. This may be due to the better than normal corrosion protection offered by the lead-free high-phosphorus bath, and more testing is required to compare the ternary alloy with a conventional lead-based process.

Figure 5—*Aluminum panel plated with a 25-µm (1.0-mil) Ni-P-Sn deposit, after 2000 hr NSS.*

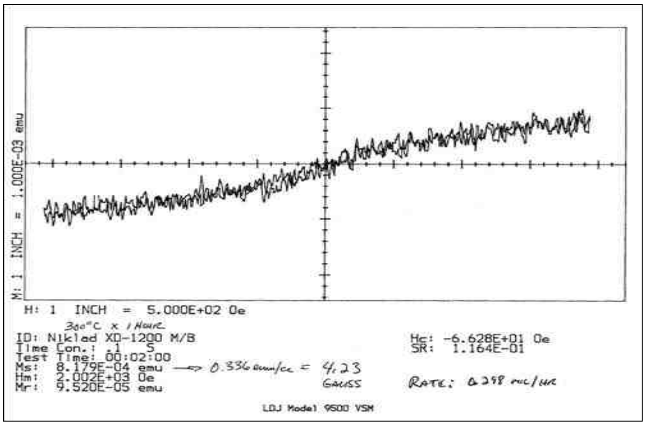
Figure 7—*20-µm ternary alloy after 200 hr CASS.*

Finally the deposit is extremely resistant to nitric acid. A user in Asia has a requirement for resisting 50% nitric acid for in excess of 4 hr. This has been achieved. In fact, they have at times obtained in excess of 8 hr without significant darkening of the deposit, allowing them to approach a completely new market for electroless nickel.

Field experience has indicated that in reality the deposit gives a much higher level of corrosion resistance than conventional high-phosphorus deposits, as indicated by the corrosion results seen in laboratory and accelerated tests, especially when tested on aluminum substrates.

Magnetic properties

The deposit as plated is non-ferromagnetic (Fig. 8) and shows excellent resistance to the development of magnetism even when heated. When heated at 320°C for 1 hr, there is no development of intrinsic magnetism. This leads to a belief that the crystallization temperature may be different from a conventional 10 -12 wt% P process, and hence some work was carried out using differential scanning calorimetry. This is reported later in the paper.



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ID: Niklad XD-1200 M/B
Time Con.: .1   S
Test Time: 00:02:00
Ms:  8.179E-04 emu
Hm:  2.002E+03 Oe
Mr:  9.520E-05 emu
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Hc: -6.628E+01 Oe
SR:  1.164E-01
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Figure 8—*Magnetism of ternary alloy.*

Ductility

The deposit shows very high ductility when compared to conventional high-phosphorus EN deposits. This can be seen by the amount of deformation which can be imparted onto a foil or a plated component without cracking of the deposit. An experiment to measure the ductility was devised by measuring the amount of elongation that can be applied to an annealed copper strip before the EN cracks. Figure 9 shows the ductility results of a 20-μm ternary alloy deposit.

Figure 9—*Ductility results for a 20-μm ternary alloy bent over a 12.5-mm mandrel.*

Hardness and wear resistance

The hardness of the alloy is seen to be very slightly lower than a conventional deposit with equivalent phosphorus, as seen in Fig. 10. This is expected as the presence of the tin would be expected to make the deposit softer. However, the difference is small enough to be within experimental error. Heat treatment increases the hardness (Fig. 11) but the results are slightly lower than if the deposit were just a nickel phosphorus alloy. An older bath is also slightly softer after heat treatment, due to the slightly higher tin content in the older solution.

The effect of heat treatment on the wear resistance, using the Taber Wear Test, is interesting (Fig. 12). The results show that the weight loss is less than an equivalent high-phosphorus deposit, both as-plated and with heat treatment but as the solution ages, the effect of heat treatment reduces the advantage until the deposits perform in the same way.

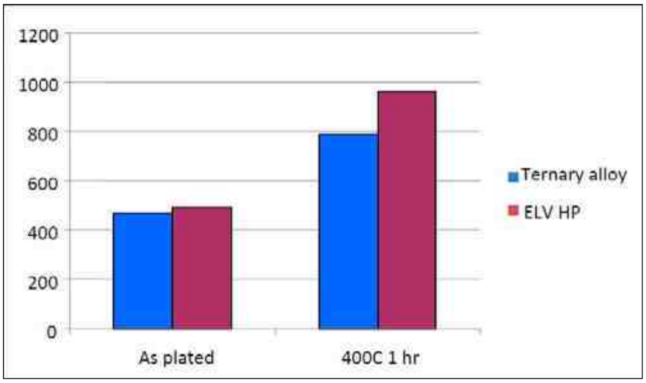

Figure 10—*Hardness of deposit compared with a conventional lead-free process.*

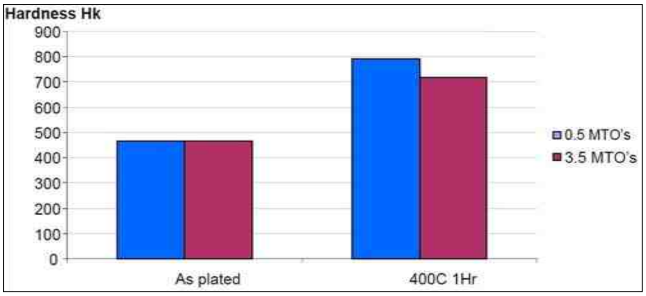

Figure 11—*Effect of heat treatment on hardness.*

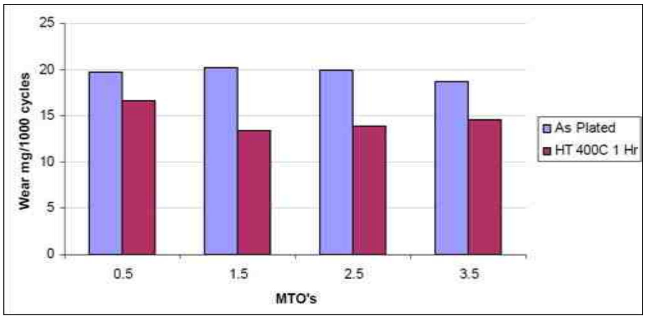

Figure 12—*Taber wear results for the ternary deposit and the effect of heat treatment.*

Effect of heat treatment on metallurgical structure

As the deposit shows different performance after heat treatment, it was expected that there would be a difference in the temperature at which the deposit crystallizes. To measure this, two foils, one from a conventional lead-stabilized high-phosphorus EN and one from the ternary alloy process, were tested using differential scanning calorimetry (DSC). The results are shown (Fig. 13). Interestingly, there is no difference in the temperature at which crystallization occurs, meaning that the tin in the alloy is not involved in this process. No phase diagrams for this particular alloy could be found to explain this and so further study could be useful.

Solution operation

The plating bath is very different to operate when compared to other conventional electroless nickels, due to the difficulty in maintaining the tin concentration in the solution. The operation is therefore not suitable for all existing platers of electroless nickel as certain facilities are necessary to ensure the quality which can be achieved from the process. This involves ensuring that the equipment is set up correctly and prescribed maintenance procedures are followed. However, if this is done, then the quality of the deposit and the improved performance offered more than compensates for the extra effort.

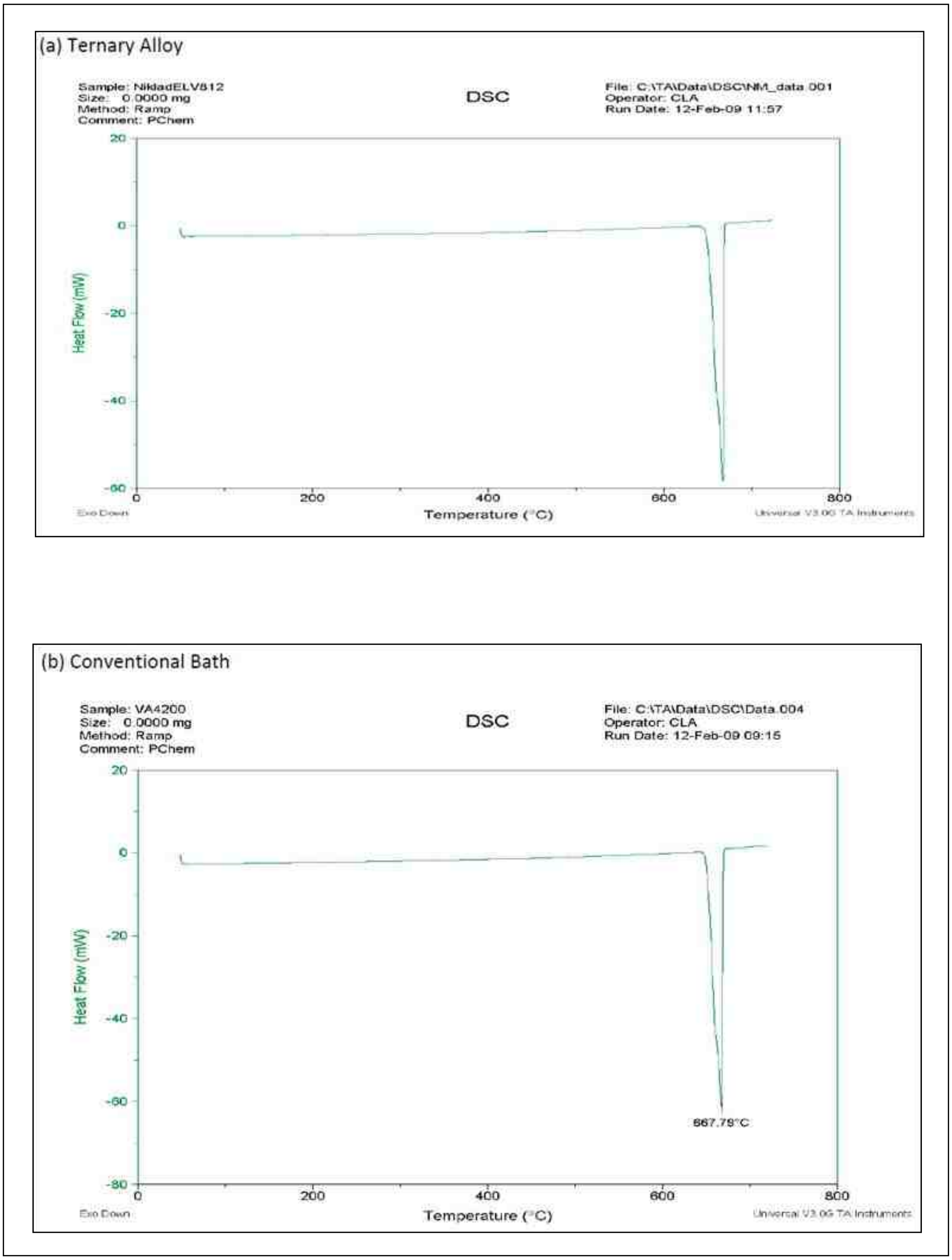

Figure 13—*Effect of heat treatment on the crystallization of the deposit compared to a conventional lead-containing high phosphorus: (a) ternary alloy, (b) conventional bath.*

Conclusion

The use of a ternary electroless nickel process provides a deposit that potentially has advantages over existing high-phosphorus deposits in offering superior corrosion resistance, with no loss of performance in wear applications. However, as they are more difficult to operate and expensive to use, in order for ternary deposits to become well established in the market, these advantages may need to be fully quantified.

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About the author

Duncan Beckett is the Global Marketing Manager for Engineering Coatings at MacDermid. Duncan has an honors degree in Chemistry, which was gained while working as a chemist at a large job shop plater before becoming the Technical Manager in the same company. The main part of the business was EN and EN/PTFE, and he was also involved in most other electroplated finishes and fluoropolymer coatings. He was employed by Canning as an Applications specialist, and joined MacDermid after their acquisition of Canning in 1998. At MacDermid he worked as the Product Manager for electroplated coatings in Europe before starting his present job in 2006.

People in the News

Robert Smith Joins Enthone as Eastern Canada Regional Manager

Mr. Robert Smith has been named Eastern Canada Regional Manager by Enthone Inc., a business of Cookson Electronics (West Haven, CT). He is responsible for managing the growing Enthone sales and technical service team that has been firmly established over the last year.

Mr. Smith comes to Enthone with nearly forty years experience in the metal finishing industry. A long-time member of AESF and NASF, he most recently served as the General Manager for Torcad Limited in Toronto. Previously, Mr. Smith was with Atotech Canada, where he served in sales management, technical support and operations roles.

Educated in England, Mr. Smith earned an O.N.C. diploma in chemistry from Welwyn Garden City College of Further Education, as well as an H.N.C. in chemistry from Hatfield Polytechnic Institute.

The appointment of Mr. Smith demonstrates Enthone's commitment to the Canadian market and, more specifically, its Canadian customers and partners. Last year Enthone acquired exclusive rights and knowledge to all intellectual property of Ontario-based Westbrook Technologies relating to the surface finishing industry. Earlier this year, Enthone announced it had become the Canadian distributor for Dipsol America. ***P&SF***

Answers to I.Q. Quiz #460

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1. Minimizing airborne hexavalent chromium mists.
2. FALSE. Among other instruments, a spiral contractometer is used.
3. High porosity and low abrasion resistance.
4. FALSE. Galvanic Series
5. TRUE.