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Operational Experience Using an Organically-Stabilized Electroless Nickel

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Electroless nickel deposits have historically used heavy metals as stabilizers and brighteners, to give bright and easy-to-use processes. This paper will review the experiences gained in using an organically-stabilized bath at customers with a range of production environments. The properties compared include plating speed, brightness, phosphorus content, stability and activation on a range of substrates, and seeks to compare these to other traditional processes. It will also assess the performance of the deposit in tests such as electrochemical and salt spray corrosion, hardness and wear.

Introduction

Electroless nickel (also known as chemical nickel) has become a major part of the surface finishing industry due to its technical features of deposit thickness consistency, corrosion resistance, corrosion protection, hardness, wear resistance and many others. The process relies on chemical reduction of the nickel that must be controlled to avoid plating of the tanks and equipment (plate out) or decomposition of the chemistry. The baths require additives to control this reduction that are commonly known as stabilizers. The baths are not specularly bright as originally plated and so brighteners are also required, often the additives used to provide stability are the same as those used to provide brightness.

Lead and cadmium have been the industry standards to provide both brightness and stability for the full range of electroless nickel processes over the last 30 to 40 years.[1] In the last five years, due to the passage of legislation to improve the ease and ability to recycle products, (mainly from the European Union, but increasingly from other countries such as U.S.A., Japan and Korea[2]), the use of these additives is now controlled in such a way that alternatives have been required to replace them. Although the main legislation (RoHS, ELV and WEEE) allow the use of limited amounts of lead and cadmium, in reality these limits have meant that the use of lead is possible but cadmium is not for most electroless nickel processes. Many people, therefore, have continued to use semi-bright baths using just lead as a stabilizer.

Despite the existing legislation, there is an increasing demand to remove lead completely, driven by specifications such as NSF 51,[3] and corporate law (Volvo Black list STD 100-0002) and this has resulted in the expansion of electroless nickel processes formulated to be lead- and cadmium-free over the last five years.

It is an interesting fact that MacDermid's experience is that the market for cadmium- and lead-free processes is now greater than 30% and increasing, of the total electroless nickel market in Europe, the Americas and Japan. There is also growing interest in these products from China and India.

The replacement processes have often reverted to the use of bismuth, which was one of the original metallic stabilizers used in electroless nickel.[1] Interestingly bismuth was replaced over time with lead and cadmium, as products with these stabilizers were perceived as giving better performance.

The use of bismuth has been related to issues with the activation of certain substrates, and the cause of high tensile stress in deposits, so the move back to it as a primary stabilizer has not been an unmitigated success. Although bismuth is classified as Class B, as one of the many materials on the JGPSSI (Japan Green Procurement Survey Standardization Initiative) list,[4] there are no specific environmental issues with its use in electroless nickel processing in the U.S.A. or Europe. However, Japan has been asking for electroless nickel processes which contain no metals other than nickel, and this demand is becoming ever more urgent.

These processes have been researched now for more than two years and a paper on the development process was published in 2007.[5] This article discusses the actual performance of these baths at customers in full production environments, and outlines the advantages and potential disadvantages of this type of technology.

A full range of products are now available with organically-stabilized chemistry. These include high phosphorus (10 to 12 wt%), medium phosphorus (7 to 9 wt%), low-mid phosphorus (4 to 7 wt%) and a low phosphorus bath (1 to 3 wt%). All but the high

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phosphorus bath have been proven in production environments covering a wide range of operational experience. This article focuses on the 4 to 7 wt% phosphorus bath as this forms the largest market presently used in the USA today.

The performance of the plating solution is reviewed based on experience from many different "job shop" platers. It consists of the plating solution performance in terms of ease of use, speed of plating, consistency of operation, stability in operation, activation of the plating and bath life. The performance of the deposit is evaluated differently and is reviewed in terms of wear resistance, hardness, corrosion resistance, stress and gloss.

Operational performance

The plating solution has been used in a wide range of applications and has proven itself as an alternative to metallically-stabilized processes over the last 12 months.

Plating tanks

The bath is used at customers in both polypropylene and stainless steel tanks (either only nitric passivated or anodically protected) without technical issues. It is standard only to clean and passivate an anodically-protected stainless steel tank after every solution (seven or more MTOs) and this has also been the case with the organically-stabilized bath. There has not been any perceived advantage or disadvantage in moving away from metal-stabilized chemistry.

With polypropylene, it is slightly different. One of the users of the process has an old, scratched and damaged polypropylene tank into which the solution is transferred after four MTOs of operation in a stainless steel tank. With the metal-based ELV technology, this tank used to plate up daily, and it now can be used for three days before cleaning is required.

Another interesting fact is that it is quite normal to add extra metallic stabilizers when using anodically-protected stainless steel to compensate for any stabilizers plated onto the cathodes in the solution. The effect of this is that special additives or modified solutions are often required, when compared to solutions used in polypropylene tanks. With the organic bath, this has not been necessary, as the same chemistry is suitable for both polypropylene and stainless steel operations.

Substrate effects

Some of the new ELV-compliant chemistry has been found to have activation issues when plating difficult steel substrates (*e.g.*, with a high lead content), copper and brass (activated in the plating solution) and aluminum. This is thought to be due to the lower solubility of the non-lead stabilizers in the plating bath that makes the initial activation slower from a more strongly absorbed species.

Using organic stabilizers has resulted in fewer activation issues, although where customers use palladium, initiation on copper and brass rather than on a nickel strike (either internally in the solution or externally before the electroless nickel) is still not as good as using either a lead- or bismuth-stabilized process.

One advantage has been its life on aluminum. Without an initial strike bath, it is not normal to plate more than four MTOs on aluminum due to the increased risk of adhesion failure. One of the customers using the bath plates a wide range of substrates including aluminum, and has found that it could still plate on wrought alloys to 4.5 MTOs and on cast alloys to seven MTOs.

The reasons for this are not known. However there are two factors that may influence this:

1. A possible increased tolerance to metallic contamination.
2. The low stress in the bath as it ages.

More work is required to determine the exact reasons for the advantages. Although long bath lives can be achieved in laboratory tests, it is a more accurate reflection of the bath performance to see this in an actual working environment. The process will continue to be tested to see if these life limits can be increased even further in the future, but already we see positives. As many of these aluminum parts are powder-coated at 450°F after plating, the adhesion test is quite extreme.

Additive stability

An advantage of removing heavy metal stabilizers from the plating bath is that it is not necessary to use strong complexants to maintain them in solution, due to their limited solubility and their low solubility with certain sulfur-containing additives. These complexants include EDTA or derivatives of EDTA, some of which are banned in countries such as Germany.

The result of this is that the spent solutions are more difficult to waste treat than is normal for nickel solutions without a strong chelator. As the new solutions do not use metals, there is no requirement to use these strong complexants in the bath. Even while using these complexants, the shelf lives of many of the ELV chemistries are not as long as those of conventional systems. Trace impurities from some of the raw materials used in the process chemistry, such as silicates and phosphates, can mean that the metals slowly precipitate. The effect of this is inconsistent performance depending on where in the container the additives were drawn - the definition of a short shelf life. This is worse when using bismuth as it has a very limited solubility in many forms, and can precipitate as a dark fine particle or colloid.

Plating speed

The organic bath shows good speed that lasts throughout its life, as against conventional solutions which slow down as they age. This is partly a function of the basic chemistry, but also due to the need, with metallic stabilizers, for the metal concentration to rise slowly as the bath ages, as well as the natural inhibiting effect of absorbed metal ions. The high speed offers some advantages, but it is not always possible to take advantage of the increased production throughput (Fig. 1).

In order to maintain a high speed, it is important to ensure that the pH is kept high, greater than 5.0. The advantage of this is that if the bath needs to be slowed down (as we have found in some operations), then the temperature can be reduced. A customer using the bath found that at more than 1 mil/hr, production could not keep pace with it and so slowed the bath down to 0.8 mil/hr. This meant they could reduce the temperature to 185°F, and still maintain a very good plating rate. This has very positive implications for the cost of heating, as they could reduce the temperature by more than 10 F° and still obtain a higher rate than previously.

Control

A major advantage for the operation of organic baths is the lack of sensitivity to large additions, when compared to metal-stabilized solutions. A customer who was operating at 3.0 g/L nickel with this solution, allowed the bath to fall to 1.2 g/L nickel, and then added back the 60% addition required to bring the solution back up to strength in one large addition. In a metallically-stabilized solution, this would have resulted in skip plating at best but probably

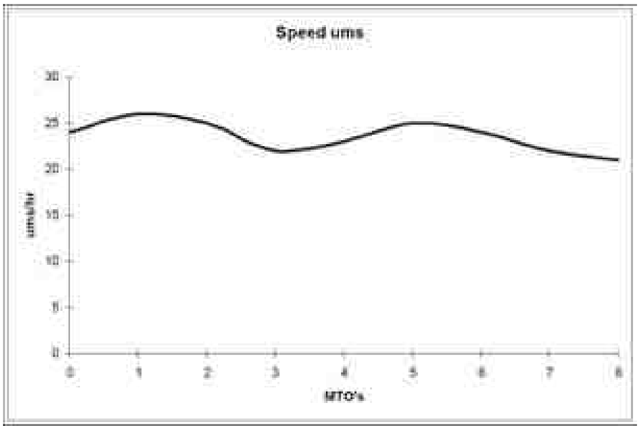

Figure 1—EN deposition rate versus age of the bath.

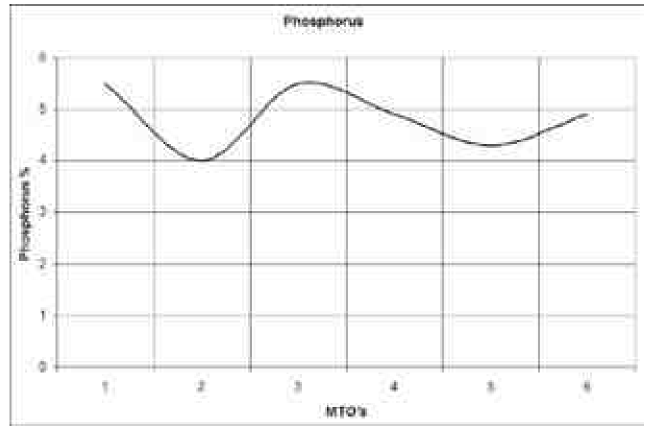

Figure 2—Phosphorus content versus age of the bath.

it would actually stop plating, whereas with the organic bath, the solution continued to plate normally. This is very positive when using the bath as a low metal operation,[6] as it means that auto-dosing is not a requirement to operate below 6.0 g/L as a standard at present.

There is also an effect when a customer is operating with low (less than 0.1 ft^2/gal) bath loadings. The normal slowing down of the solution due to the constant low loading is not an issue. Conversely, using much higher bath loadings such as above 1.5 ft^2/gal, are still acceptable.

However, all of this does not mean that the customer can reduce the level of control with the plating solution. Like all plating baths, they perform best when operated within very tight parameters, ideally between 90 and 105%.

Deposit properties

The as-plated deposit looks slightly different from conventional- and metallically-stabilized systems. It exhibits a "whiter," less yellow deposit. This is because of a lack of metallic stabilizer being co-deposited, which can be as high as 0.15 wt% if cadmium and lead are used, versus 0.1 wt% if using bismuth, although the surface structure of the deposit is unchanged from a conventional bath.

The only materials co-deposited with the phosphorus and nickel are carbon and sulfur with the low, low-medium and medium phosphorus systems, and carbon with the high phosphorus bath. Work is continuing on determining the amounts being plated into the EN deposit but these are not available at the time of this writing.

Phosphorus content

The bath shows a low-medium level of phosphorus throughout its life, with the level falling slightly as the bath ages. If the solution is operated as an LMO™, then the phosphorus content will tend to be slightly higher, but following a similar pattern (Fig. 2).

Hardness

The deposit obtained from the organic bath is harder than that from a genuine medium phosphorus bath, as shown in Fig 3.

Wear resistance

Wear resistance, as measured using a Taber Wear Test, is reduced in line with the extra hardness realized. This can be seen in Fig. 4.

Corrosion resistance

The corrosion resistance of the deposit was initially tested using electrochemical means. This method tests the speed at which the deposit corrodes in set conditions, normally using a 5% sodium chloride or a 10% sulfuric acid solution.

In these tests the deposit was found to be as good as conventional systems with slightly higher phosphorus content. Neutral salt spray testing was then carried out to confirm these results.

Results when the bath was new were very good, but they did give slightly worse results as the solution aged. This is seen as a result of increased porosity and number of coating defects, since corrosion exposure tests are as much a test of the porosity of the deposit as of the inherent resistance offered by the nickel.

In practice at customers, parts have been tested side by side with lead- and cadmium-based materials, and gave the same number of hours of resistance on actual components.

Stress

One reason for the good corrosion resistance is that the bath does not exhibit any sign of high tensile stress throughout the bath life. It starts off slightly tensile and slowly becomes less tensile and sometimes even crosses over to the compressive side. This is a function of managing to control the phosphorus content from the bath and maintaining the speed of the solution throughout its life.

It is also a factor in assessing the ability of the bath to continue to plate good quality deposits as it ages. The main limiting factor is the growth of tensile stress from conventional systems, especially medium- and high-phosphorus deposits. Low levels of stress mean that good deposits are produced throughout the bath life, as in Fig. 5.

Appearance

Although having little effect on the actual performance of the deposit in application, the brightness of the bath is still a major contributor to the perception of quality. Rarely do you come across an application where more dullness is required (but it has happened). The organically-stabilized chemistry can produce bright deposits, but it is not yet at a standard where it completely matches the cadmium- and lead-brightened processes. What has been noted is that the gloss/brightness of the deposit does not change as much as with conventional systems, and is quite consistent for the life of the solution. This can make it more useful, as it means that work does not have to be held back as the solution may be at the end of

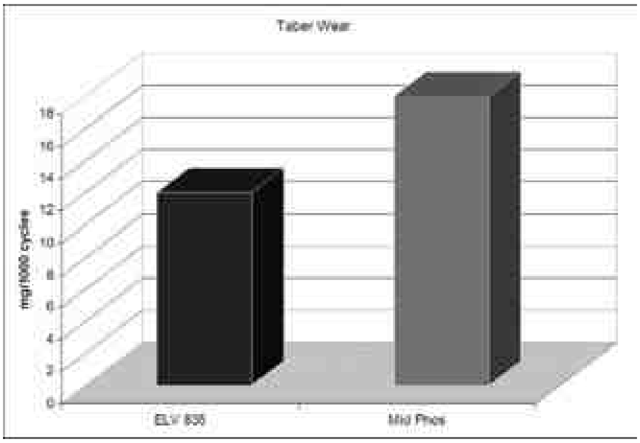

Figure 3—Comparison of hardness of an organic and a conventional mid-phosphorus deposit.

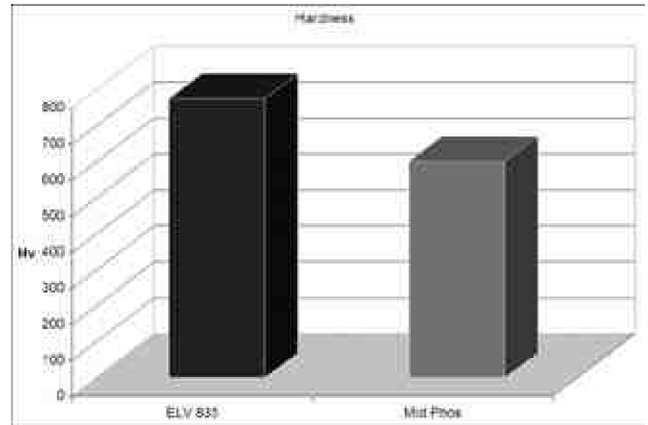

Figure 4—Comparison of wear resistance of an organic and a conventional mid-phosphorus deposit.

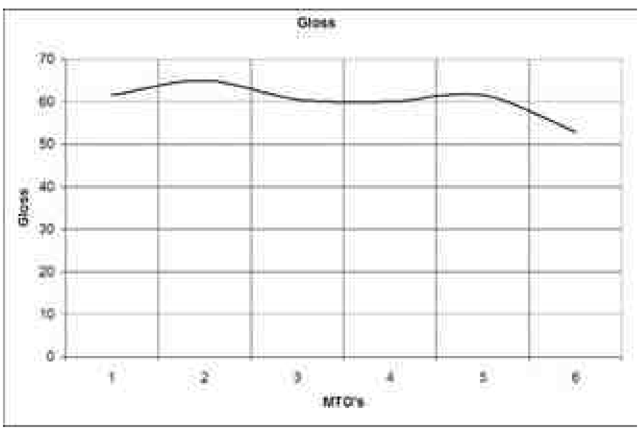

Figure 5—Gloss rating versus age of the bath.

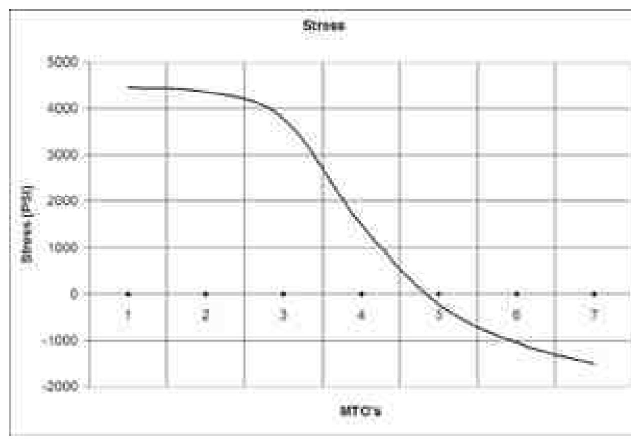

Figure 6—Deposit stress versus age of the bath.

the bath life, awaiting a new solution to be made up to plate the relevant parts (Fig. 6).

Conclusions

It is possible to use and implement successfully a range of electroless nickel plating solutions that do not use any heavy metals other than nickel in the formulations in a range of production environments. These baths already offer some advantages over conventional systems and will undoubtedly improve as further experience becomes available from customers. More importantly, this means that they are unlikely to be effected by future legislation concerning the use of controlled metals and other substances in the foreseeable future.

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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.