Operational Experience Using an Organically Stabiliser Electroless Nickel

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Abstract

Electroless nickel deposits have historically used heavy metals as stabilisers and brighteners, to give bright and easy to use processes.
This paper will review the experiences gained in using an organically stabilised bath at customers with a range of production environments. The properties compared include plating speed, brightness, phosphorus content, stability, 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.

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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 stabilisers. 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 – 40 years(1). In the last 5 years, due to the passing of legislation to improve the ease and ability to recycle products, (mainly from the European Union, but increasingly from other countries such as USA, 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 stabiliser.

Despite the existing legislation, there is an increasing demand to completely remove lead, 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 5 years.

It is an interesting fact that MacDermid's experience is that the market for cadmium and lead free processes is now >30% and increasing, of the total Electroless nickel market in Europe, 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 stabilisers used in Electroless Nickel(1), interestingly Bismuth was replaced over time with lead and cadmium, as products with these stabilisers perceived as giving better performance.

The use of bismuth has been related to issues with activation of certain substrates, and the cause of high tensile stress in deposits, so the move back to it as a main stabiliser has not been an unmitigated success.

Although Bismuth is classified as Class B as one of the many materials on the JGPSSI(4) list, there are no specific environmental issues with its use in Electroless Nickel processing in the USA or Europe. However, Japan has been asking for Electroless Nickel processes which contain no other metals than Nickel, and this demand is becoming ever more urgent.

These processes have been researched now for more than 2 years and a paper on the development process was presented in 2007(5). The current paper will discuss the actual performance of these baths at customers in full production environments, and outline the advantages and potential disadvantages of this type of technology.

A full range of products are now available as organically stabilised chemistry, these include high phosphorus (10 – 12%), medium phosphorus (7 – 9%), low mid phosphorus (4 – 7%) and a low phosphorus bath (1 – 3%). All but the high phosphorus bath have been proven in production environments covering a wide range of operational experience. This presentation will focus on the 4 – 7% phosphorus bath as this forms the largest market presently used in the USA today.

The performance of the plating solution is reviewed based upon 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 as 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 alterative to metallically stabilised 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 to only clean and passivate an anodically protected stainless steel tank after every solution (7 or more MTO’s) and this has also been the case with the organically stabilised bath. There has not been any perceived advantage or disadvantage in moving away from metal stabilised 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 4 MTO’s of operation in a stainless steel tank. With the metal based ELV technology this tank used to plate up daily, now it can be used for 3 days before cleaning is required.

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

Substrates Effects

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

Using organic stabilisers has resulted in less activation issues, although where customers use palladium initiation on copper and brass rather than nickel strike (either internally in the solution or externally before the Electroless Nickel) it is still not as good as using either a lead or bismuth stabilised process.

One advantage has been its life on aluminium. Without an initial strike bath it is not normal to plate more than 4 MTO’s on aluminium due to the increased risk of adhesion failure. One of the customers using the bath plates a wide range of substrates including aluminium, and found that it could still plate on wrought alloys to 4.5 MTO’s and on cast alloys to 7 MTO’s.

The reasons for this are not known, however there are 2 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 aluminium parts are powder coated after plating at 450°F, the adhesion test is quite extreme.

Additive Stability

An advantage of removing heavy metal stabilisers 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 sulphur-containing additives. These complexants include EDTA or derivatives of EDTA, some of whom 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 for these strong complexants to be used as part of the bath.
Even while using these complexants, the shelf life of many of the ELV chemistries are not as long as 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 stabilisers for the metal concentration to slowly rise 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 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 1mil/Hr production could not keep pace with it and so slowed the bath down to 0.8mils/Hr. This meant they could reduce the temperature to 185^{o}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^{o}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 compared to metal stabilised solutions. A customer who was operating at 3g/L nickel with this solution, allowed the bath to fall to 1.2g/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 stabilised solution this would have resulted in the bath skip plating at best but probably it would actually stop plating, whereas with the organic bath the solution continued to plate as normal.

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 6g/L as standard at present.

There is also an effect when a customer is operating with low (<0.1ft^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 >1.5ft^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 – 105%.

Deposit Properties

The bath as plated looks slightly different to conventional and metallically stabilised systems; it gives a “whiter”, less yellow deposit.

This is due to the lack of metallic stabiliser being co-deposited, which can be as high as 0.15% if Cadmium and Lead are used, as against 0.1% if using Bismuth, although the surface structure of the deposit is unchanged to a conventional bath.

The only materials co-deposited with the phosphorus and nickel are carbon and sulphur 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 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 achieved from the organic bath is harder than that from a genuine medium phosphorus bath, as shown below in Fig 3.

Wear Resistance

Wear resistance, as measured using a Taber Wear Test, is reduced in line with the extra hardness seen. This can be seen in Fig4.

Corrosion Resistance

The corrosion resistance of the deposit was initially tested using electrochemical means. This tests the speed at which the deposit corrodes in set conditions, normally using a 5% sodium chloride or a 10% sulphuric 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 corrosive 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 signs 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. 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 stabilised 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 commented is that the gloss/brightness of the deposit does not change as much as 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 the end of the bath life, awaiting a new solution to be made up to plate the relevant parts. Fig 6.

Conclusions

It is possible to use successfully implement 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 become 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.

References

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(6) Electroless Nickel: Beyond ELV Mike Barnstead: March 2007 Products Finishing

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Fig 1.

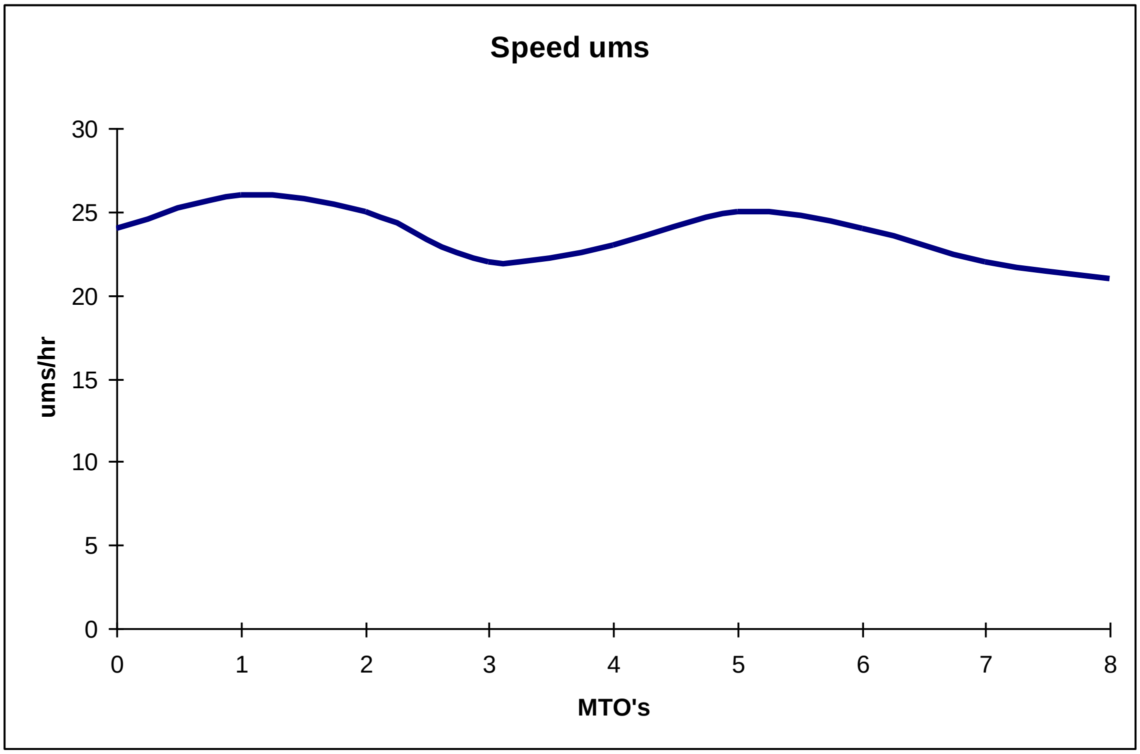


Fig 2.

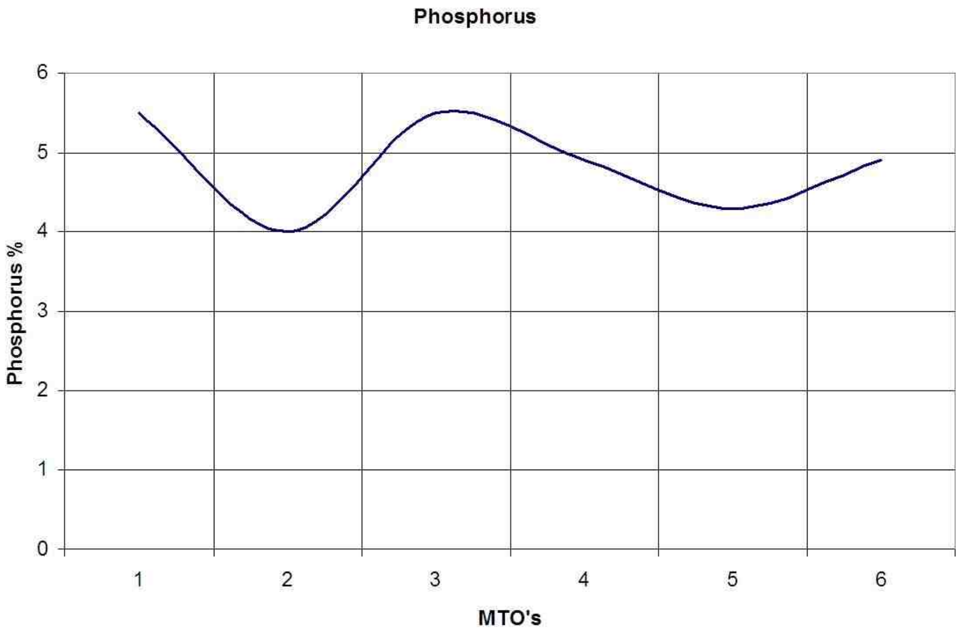

Phosphorus
Phosphorus %
0
1
2
3
4
5
6
MTO's
1
2
3
4
5
6

Fig 3.

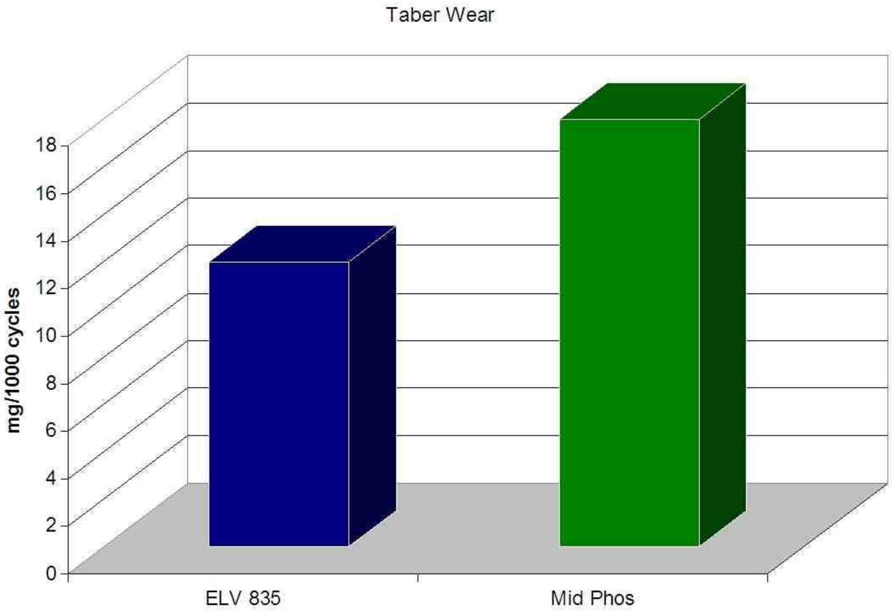

Taber Wear
mg/1000 cycles
0
2
4
6
8
10
12
14
16
18
ELV 835
Mid Phos

Fig 4.

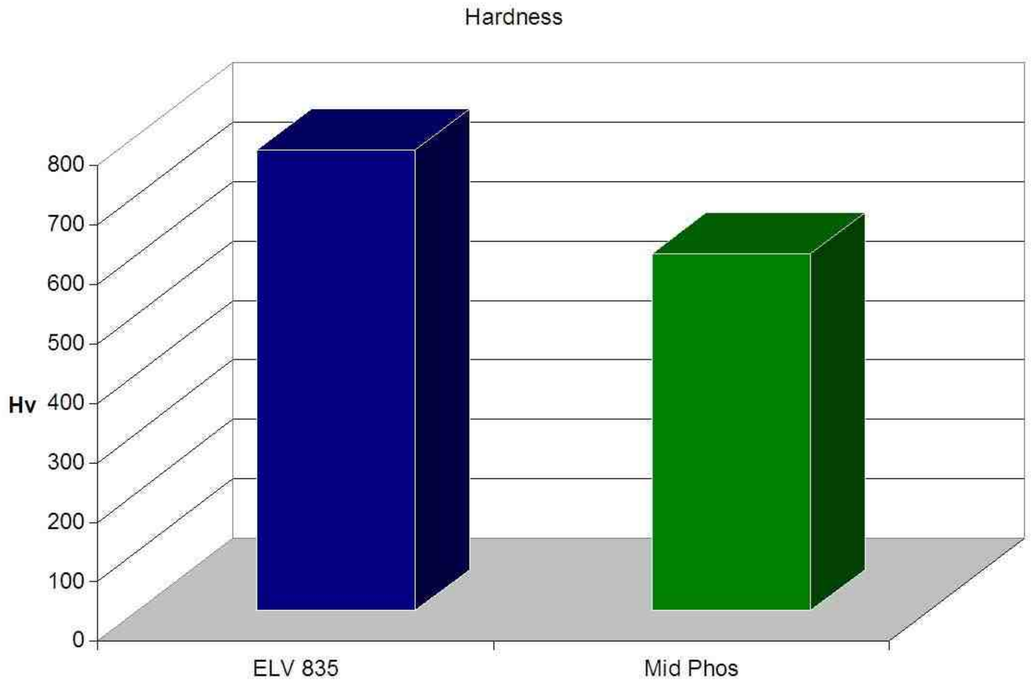

Hardness
Hv
800
700
600
500
400
300
200
100
0
ELV 835
Mid Phos

Fig 5.

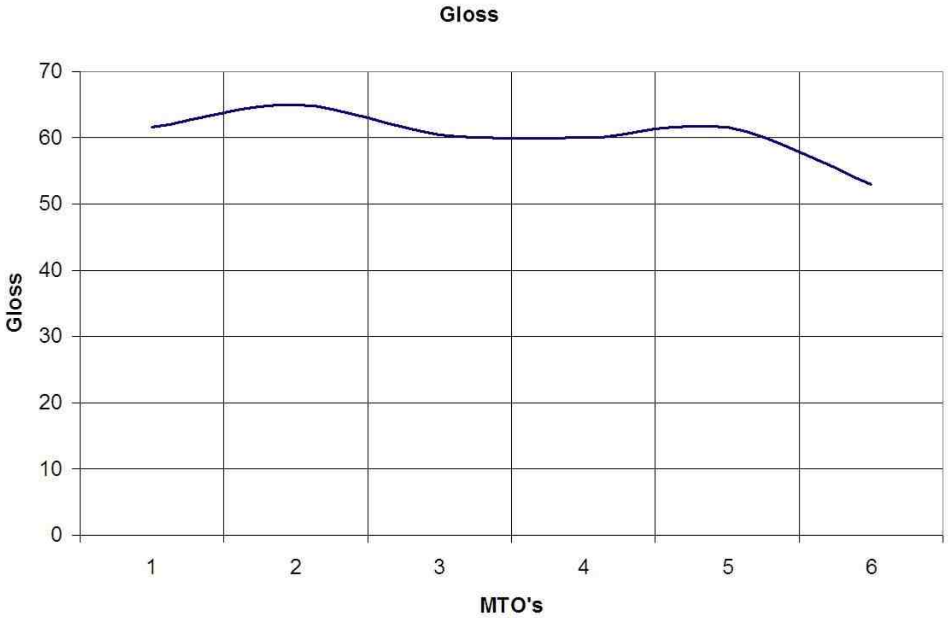
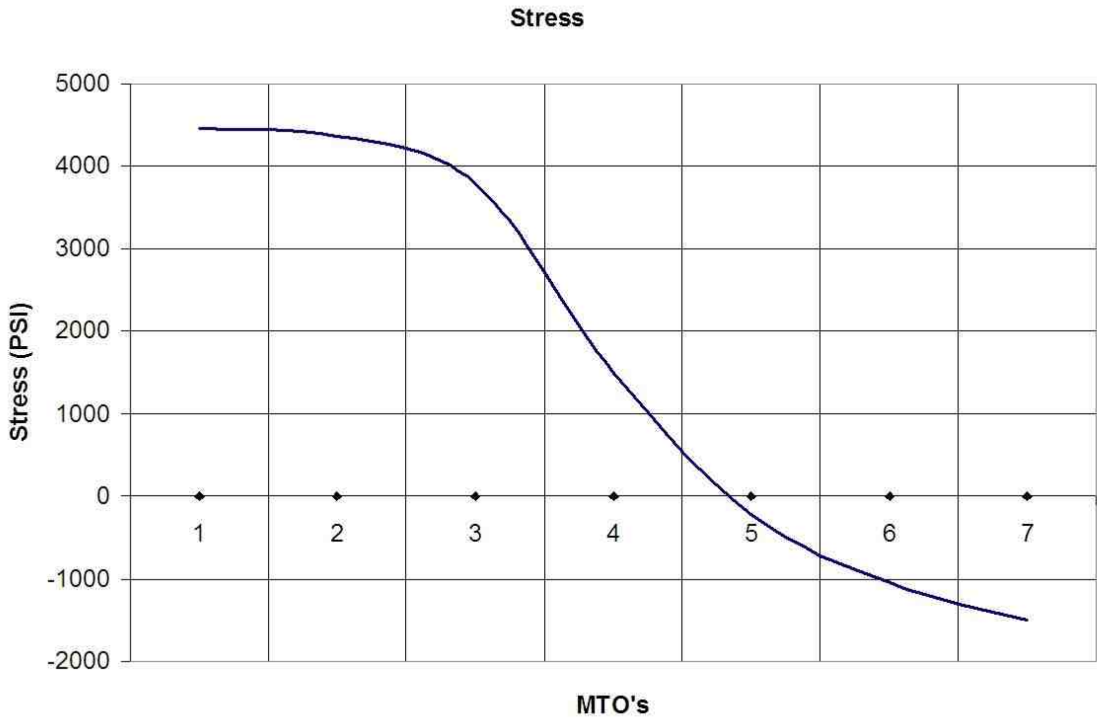

Gloss
Gloss
70
60
50
40
30
20
10
0
1
2
3
4
5
6
MTO's

Fig.6



Biography

Duncan Beckett is the Global Marketing Manager for Engineering Coatings at MacDermid. Duncan has an honours degree in Chemistry which was gained whilst working as a chemist in 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 2 years ago.

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