Lead and Cadmium free Electroless Nickel for End-of-Life Vehicle Directive

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The End-of-Life Vehicle Directive (ELV) is designed to remove certain hazardous materials from automobiles and their components. These substances are hexavalent chromium, lead, cadmium and mercury. Typical electroless nickel formulations contain lead and cadmium for stability and brightness and these elements readily co-deposit into the EN coating.

This paper will discuss a lead free high phosphorus and lead and cadmium free mid-phosphorus processes. Deposit properties and solution performance of the lead and cadmium free chemistries will be discussed and compared to conventional EN chemistries.

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Introduction

In July 1997 the European Commission presented a proposal for an European Directive on End-of-Life Vehicles (ELVs) to limit their environment impact. This ELV directive (200/53/EC) came into force in Europe in October 21, 2000. Member States of the European Union were required to set laws to reduce waste disposal generated by about 13.5 millions of ELVs each year. They must ensure where practicable the re-use, recycling and recovery of ELVs and their components and also, as a preventive action, ban certain hazardous substances. As a result materials and components in vehicles that registered after 1st July 2003 should contain no lead, mercury, cadmium or hexavalent chromium. On 27 June 2002 a Commission decision amending Annex II of Directive 2000/53/EC states: "Since it is evident that a total avoidance of heavy metals is in some instances impossible to achieve, certain concentration values of lead, mercury, cadmium or hexavalent chromium in specific materials and components should be tolerated, provided that these hazardous substances are not intentionally introduced".

In most of commercial mid P electroless nickel formulations, small amounts of various additives are introduced to ensure for example a good stability of the bath and to generate bright deposits. Lead and cadmium are commonly added to fulfill these two tasks, as they are respectively the most notorious stabilizer and brightener used in mid P EN technology. Regarding the high P electroless nickel technology, only lead is typically added in small amount to improve the stability of the bath. The problem with the ELV directive is related to these two hazardous compounds, lead and cadmium, as they are deliberately co-deposited in the Ni-P alloy to improve the characteristics of the process. As a result they should be banned from electroless nickel used in automotive applications.

These hazardous metals have to be replaced with one or more environment friendly additives. In the selection of the additives, their compatibility with the process must be first at all taken into account. They have to work in concert with the other components present in the electroless bath, i.e. the source of nickel, the hypophosphite salt, complexing agent(s) and buffer(s) to obtain deposits with the desired characteristics (P content, brightness, etc). All these components also operate in optimum concentration, temperature and pH ranges. Several additives can be found in the literature[1] and usually belong to different families, like sulfur compound, heavy metals, unsaturated organic acids, …

In regard with the mid P EN processes, the stability of the bath can easily be resolved by using a different additive than lead, but the brightness is a more complicated property to obtain without the use of cadmium. Besides stabilizer and brightener often have a synergic effect between each other and with the other compounds of the bath. Huge screening has been necessary to develop new ammonia, fluoride, lead and cadmium free mid P EN processes. Two different chemistries with different mixture of stabilizers and complexing agents will be presented in the following. The first chemistry gives a semi-bright deposit with a phosphorous content between 6 and 9 % by weight. The second one gives a bright deposit with a phosphorous content between 4 and 7 % by weight.

High P EN processes are mostly used because of their excellent corrosion resistance in acidic conditions. They have a higher corrosion resistance than the mid P processes. In addition they do not contain divalent sulfur compounds as the mid P processes do. The divalent sulfur compounds typically act as accelerator and increase the rate of the deposit in mid P processes. An increase in rate characteristically lowers the phosphorus content of the deposit, which we do not want to happen when we are looking for the highest phosphorus content in the deposit. The classic stabilizer for high P EN is lead and should be substitute. A new process has been developed. It's an ammonia and lead free high P EN process. It gives deposit with a phosphorous content between 11 and 12 % by weight.

In the following the characteristics of these three new chemistries will be presented. For the mid P processes, the interesting properties are the effect of metal turnover on: the stability, the deposition rate, the brightness, the phosphorous content, the hardness and the stress. For the high P chemistry, the most interesting properties are the deposition rate, the phosphorous content, the stress and the corrosion resistance. As only one process has been developed, its results will be compared with a conventional process that contained lead as a stabilizer.

Mid P EN processes results

Experimental Procedures

Both of these mid P electroless nickel solutions contained 6 g/L (0.8 oz/gal) Ni^{2+}, 30 g/L (4 oz/gal) sodium hypophosphite, appropriate complexing and buffering agents and various metallic and/or non-metallic additives, different than lead and cadmium. They both operated at a working temperature of 89 ± 1 °C (192 ± 2 °F). Mild air agitation was used during plating. The bath loading was kept between 0.5-2.5 dm^2/L (0.2-1.0 ft^2/gal). To be as close as industrial working conditions, the deposition rate was kept as constant as possible by adjusting the pH. Initially the pH was fixed at 4.8. Typically, it has to be increased during the life of the bath to maintain a steady rate.

For stability, deposition rate, brightness, phosphorous content and stress studies, a 55 L (15 gal) tank was used. For hardness measurements a 1 L beaker was used.
The stability was determined by aging the bath. The common term used to describe the aging of an electroless nickel bath is the so-called metal-turn-over (MTO). One MTO has passed when all the nickel originally in the bath has been consumed and replenished. A good stability of the bath is obtained when at least 3 MTO are reached without decomposition and when its characteristics (deposition rate, P content, stress, brightness,…) remain satisfactory.

The electroless Ni-P alloy was deposited on steel panels for deposition rate, brightness, phosphorous content and hardness measurements. They were pretreated anodically, rinsed in de-ionized water, activated in 25% HCl solution and rinsed in de-ionized water before deposition. After plating the samples were rinsed in de-ionized water and dried. The deposition rate of the Ni-P alloys was determined by their weight gain after one hour plating. The same samples were then visually inspected for brightness. And then they were examined by SEM/EDX for morphology and composition analysis. Hardness measurements were realized on polished crosssection of the Ni-P deposits using a Vickers microhardness tester employing a load of 0.05 kg (0.1 lb) on 50 µm (2 mil) thick deposits.

The electroless Ni-P alloy was deposited on copper test strips[2] for internal stress measurements for 20 min. Before plating, they were soak cleaned and rinsed in de-ionized water. In the electroless bath, they needed to be activated by contact with a catalytic surface. After plating, they were rinsed in de-ionized water and dried. They were weighed before and after plating.

Results

The lead and cadmium free semi-bright and bright processes demonstrated excellent stability throughout their aging study. They reached more than 4 MTO without any plating out or decomposition problem and with appropriate characteristics of the processes and the deposits.

The effect of MTO on the deposition rate for these two chemistries can be seen on *Figure 1*. First the semi-bright process behaves similarly than a conventional mid P electroless nickel bath: the pH had to be progressively increased from 4.8 at 0 MTO to 5.0 at 4 MTO in order to maintain a steady deposition rate. Second, as for the bright process, it keeps a relative constant deposition rate, 18 µm/h (0.70 mil/h), throughout the life of the bath without changing the pH. The pH was kept equal to 4.8 during all the experiment. This behavior seems like an improvement in comparison with conventional EN chemistries.

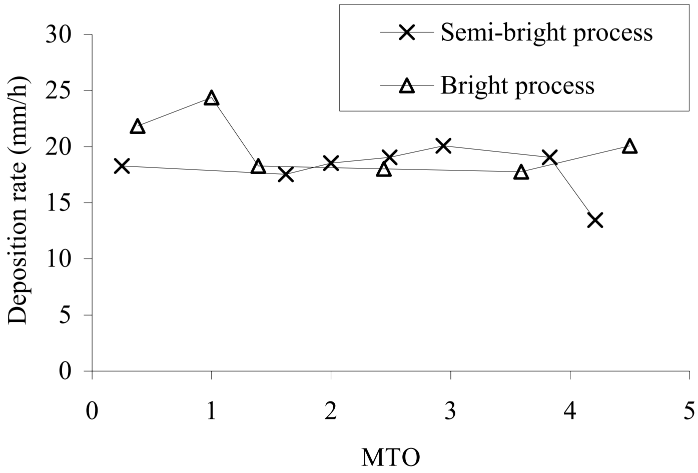

Figure 1: Effect of MTO on the deposition rate for the semi-bright and the bright processes

On *Figure 2*, the effect of MTO on the phosphorous content in the NiP alloy deposits for the two processes is shown. First, the semi-bright process gives alloys with a phosphorous content of 8.0 ± 1.0 % by weight. The P content seems to increase slightly as the bath ages. This behavior is typical of a conventional mid P EN process. Second, as for the bright process, the P content remains constant throughout the life of the bath and equal to 6.0 ± 0.5 % by weight. The P content varies within a narrower range than the semi-bright chemistry. Besides no augmentation trend is observed. This observation confirms that this new lead and cadmium free bright mid P EN chemistry brings about some improvements in comparison with a conventional chemistry.

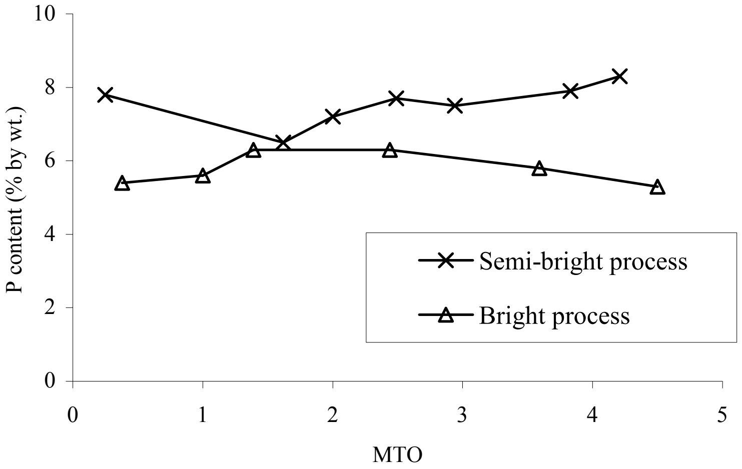

Figure 2: Effect of MTO on the phosphorous content in the deposit for the semi-bright and the bright processes

As a matter of appearance, the semi-bright process gives mate deposit from 0 MTO to 4 MTO. The bright process gives bright deposit without any brightness drop off throughout the aging study. This characteristic is another improvement in comparison with a conventional bright mid P EN process, which shows decline of the brightness after few MTO. The morphology of the deposits obtained with these baths can explain the difference in brightness. On *Figure 4* and *Figure 4*, the surface of a deposit obtained respectively with the semi-bright and the bright baths at 0 MTO can be seen: the semi-bright process gives nodular deposits, while the bright process gives smooth deposits.

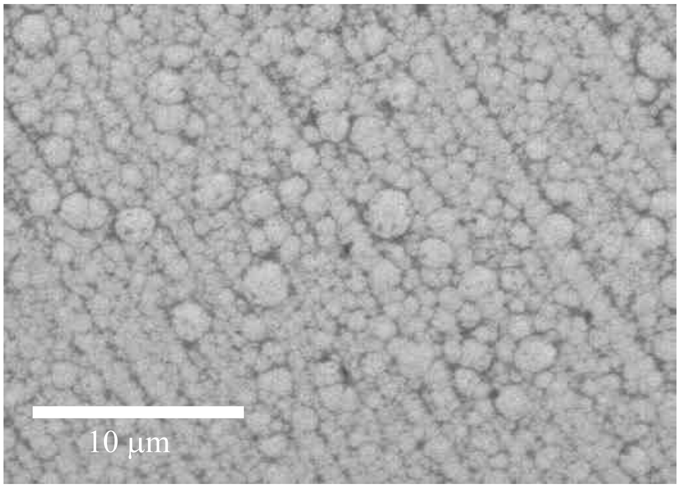

Figure 3: SEM of deposits obtained with the semi-bright chemistry at 0 MTO.

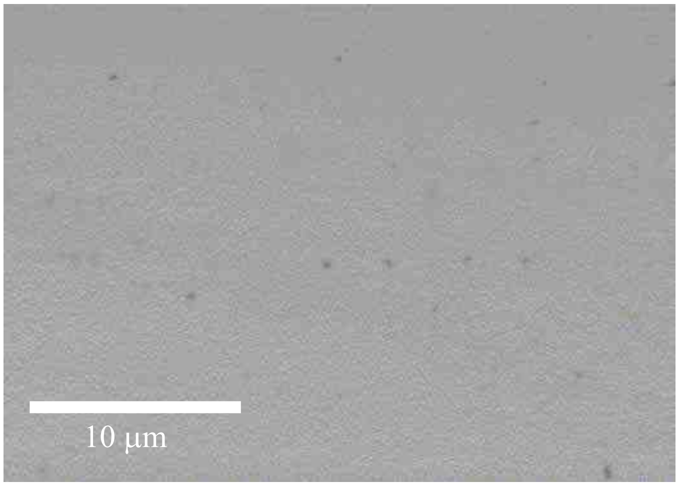

Figure 4: SEM of deposits obtained with the bright chemistry at 0 MTO.

The composition of the NiP alloy determines the hardness of the deposit: the hardness decreases when the phosphorous content increases. The effect of MTO on the hardness of deposits obtained with these two chemistries can be seen on *Figure 5*. The Vickers microhardness measurements done on deposits obtained with the semi-bright and bright chemistries give respectively 500 ± 50 HV_{50} and 600 ± 50 HV_{50}. These values are in complete agreement with the phosphorous content measurement done previously: the semi-bright process gives deposits with higher phosphorous content than the bright one. As previously, this characteristic remains constant as the bath ages for the two chemistries.

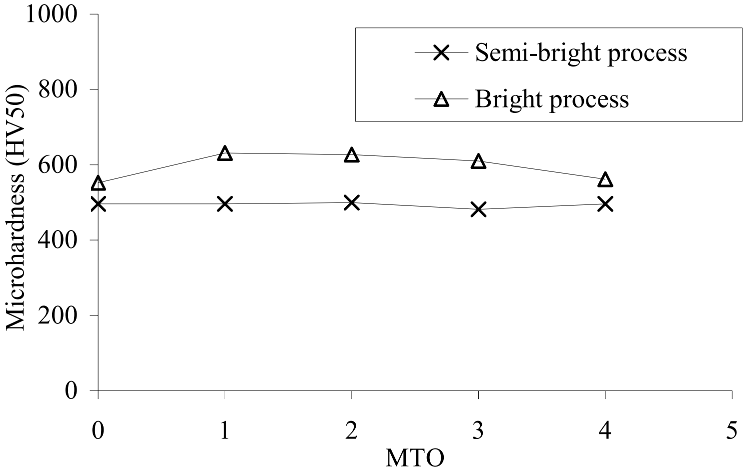

Figure 5: Effect of MTO on the hardness in the deposit for the semi-bright and the bright processes

The effect of MTO on the internal stress in the Ni-P deposits has also been studied, as the use of different additives than lead and cadmium can induce high tensile stress in the deposit. As can be seen on *Figure 6*, the semi-bright process, gives deposits with tensile stress of about 10 MPa (1450 psi) and the bright process provides deposits with compressive stress of about –20 MPa (-

3000 psi). This difference is due to the fact that different additives and complexing agents are used and also these two chemistries give different deposits in composition, especially as a matter of phosphorous content.

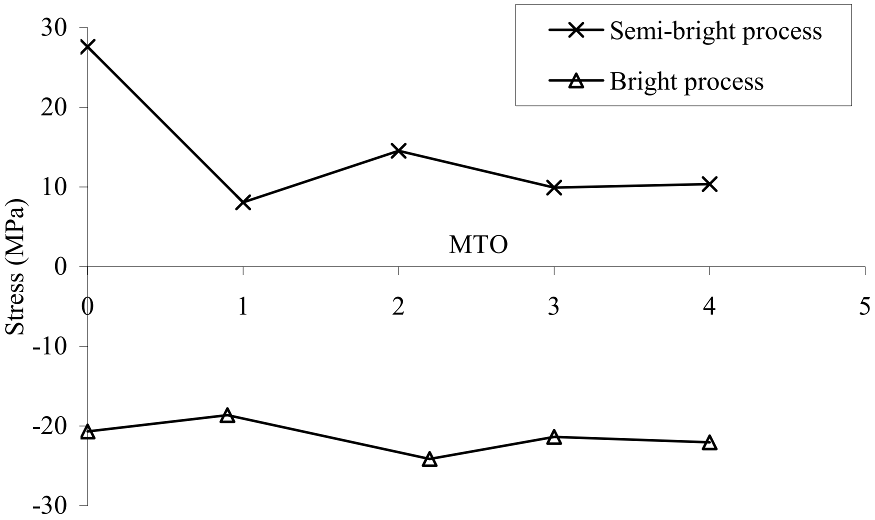

Figure 6: Effect of MTO on the internal stress for the semi-bright and bright processes

High P results

Experimental Procedures

For stability, deposition rate, phosphorous content and stress studies, a 1 L (34 oz) beaker was used. The stability was determined by aging the bath for 4 MTO.

The electroless Ni-P alloy was deposited on steel panels for deposition rate and phosphorous content. They were pretreated anodically, rinsed in de-ionized water, activated in 25% HCl solution and rinsed in de-ionized water before deposition. After plating the samples were rinsed in de-ionized water and dried. The deposition rate of the Ni-P alloys was determined by their weight gain after one hour plating. Then the same samples were examined by SEM/EDX for composition analysis.

The electroless Ni-P alloy was deposited on copper test strips[2] for internal stress measurements for 20 min. Before plating, they were soak cleaned and rinsed in de-ionized water. In the electroless bath, they needed to be activated by contact with a catalytic surface. After plating, they were rinsed in de-ionized water and dried. They were weighed before and after plating.

Results

The lead free high P process demonstrated excellent stability throughout its aging study. It reached more than 4 MTO without any plating out or decomposition problem and with appropriate characteristics of the processes and the deposits.

The effect of MTO on the deposition rate for the conventional and lead free processes can be seen on Figure 7. The lead free process behaves similarly than the conventional high P electroless nickel bath: the deposition rate decreases throughout the life of the bath. The deposition rate for the lead free process is slightly higher than for the conventional bath during all the aging study.

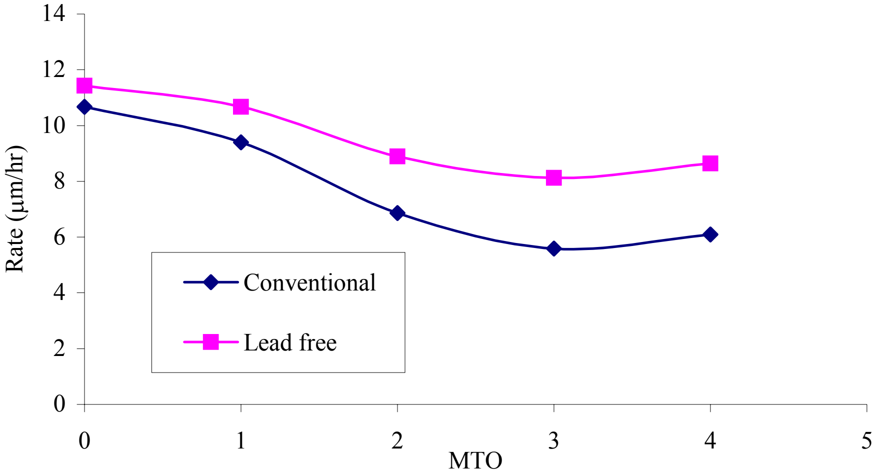

Figure 7: *Effect of MTO on the deposition rate for the conventional and lead-free processes.*

Evaluating the phosphorus content of the conventional and lead free processes they are very similar. Figure 8 shows the results. For the both processes, the P content increases slightly as the solution ages for both chemistries, in accordance with the deposition rate evolution.

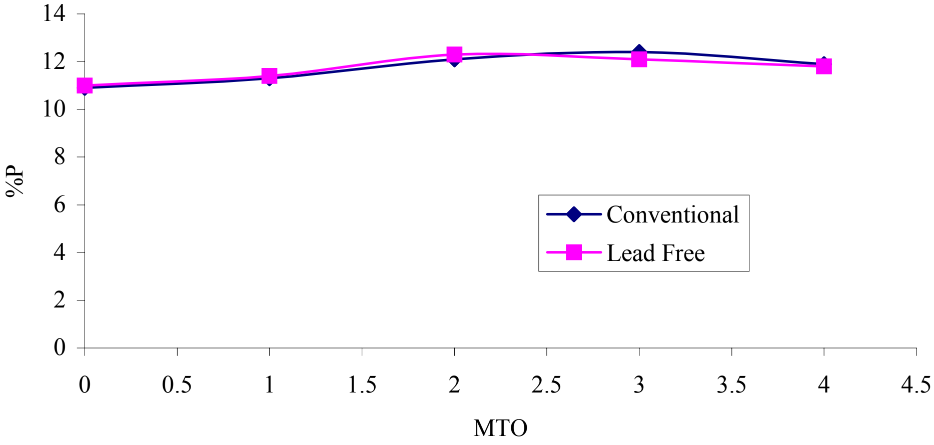

Figure 8: Effect of MTO on the phosphorous content of the conventional and lead-free processes

The effect of MTO on the internal stress for the conventional and lead-free processes can been on Figure 9. Typically high P deposits are compressively stressed and as the solution ages, orthophosphite and sulfate increases, the deposit become tensile stress.

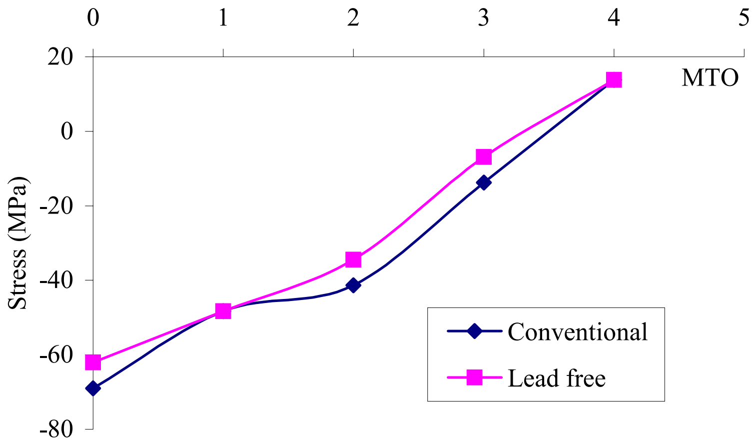

Figure 9: *Effect of MTO on the internal stress for the conventional and lead free high P process.*

Both chemistries start off between –60 to –70 MPa (-9000 to -10000 psi) compressive stress and as the solution ages to about 4 MTO the deposit converts from compressive to tensile stress.

In addition to measuring the properties of the deposit neutral salt spray testing was done on 25 µm (1 mil) deposits per ASTM 117. There was no difference in corrosion resistance between the two deposits.

Conclusion:

Environmentally safe material should not mean sacrificing quality or cost. Using hazardous materials should be avoided when developing new technologies or modifying existing technologies. This paper describes three different electroless nickel processes that do not contain lead or cadmium and have the same performance as lead and cadmium containing deposits.

Environmentally safe should mean using the best available technology to produce the best product with minimal waste and minimal use of hazardous materials.

Bibliography

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2. Berl Stein, AESF Sur-Fin 2000, (2000)