Metals Free Stabilized Electroless Nickel Processes for the 21st Century

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ABSTRACT

Specifications are increasingly requiring lead and cadmium free electroless nickel coatings for applications as diverse as automotive, electronic and food handling equipment. Several other metals that are sometimes used in electroless nickel have been listed as "Level B", materials not currently considered toxic but fit some criteria. These materials may or may not be restricted in the future. This paper discusses the properties of electroless nickel processes that are stabilized without metals and organics that might be restricted in the future. The processes have properties that make them useful today, before they might be required by regulation.

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The WEE, RoHS and ELV (1, 2, 3) regulations and the NSF/ANSI 51 (4) speak to the removal of specific materials from products and coatings. The materials discussed in these specifications that affect electroless nickel are lead (limited to 1000ppm or 0.1 wt %) and cadmium (limited to 100 ppm or 0.01 wt %). Originally the ELV regulation and the NSF/ANSI 51 specification contained the words "intentionally added". Thus, it was not possible to add lead or cadmium to a coating intentionally even if the coating content was lower than these amounts. In September 2005 these words were removed from the ELV but not from the NSF/ANSI 51. The effect is that for most electroless nickel applications lead and cadmium may be used in their traditional roles if the coating content was less than the specified amounts. However, for food and medical equipment the intentional addition of lead or cadmium is still forbidden.

In general, most high-phosphorus electroless nickel deposits meet the new ELV criterion. However, few if any of the mid-phosphorus processes that are brightened with cadmium pass.

The Japan Green Procurement Survey Standardization Initiative of July 2003 is a similar specification. The survey contains an "Attachment 1. Survey Substances List (Level A)" that notes regulation of lead and cadmium by the above mentioned specifications. The survey also contains the "Attachment 1. Survey List (Level B)". This list is titled:

Attachment 1. Survey List (Level B)
Level B
**The substance Groups of level B are those that apply to at least on of the 4 criteria stated below (*5) The criteria were decided by the discussion among JGPSSI, EIA and EICTA (on January 30-31, 2003) and the level B list is not composed of what is called hazardous substances.*
It is not a list of toxic substances.

The four criteria are listed as:
**5 a: Precious materials/substances that are present in electronics that provide economic value at the end-of-life to recyclers.*
b: Materials/substances that are of significant environmental or health and safety interest.
c: Materials/substances that would trigger hazardous waste regulatory requirements.
d: Materials/substances that could have a negative impact on end-of-life management.

The Level B list contains some metals that are used to stabilize and/or brighten electroless nickel. It also contains materials that are commonly used in electronic applications. Despite the statement "It is not a list of toxic substances" there is some concern that in the future some of these metals will join their cousins in the Level A list and be forbidden. Japanese companies, in some cases, have been asking for "non-metal stabilized" electroless nickel products because of these concerns. There are other technical reasons that also cause companies to request "non-metal stabilized" electroless nickel as well. In response to these requests several "non-metal stabilized" electroless nickel processes have been developed for high-phosphorus and mid-phosphorus applications. This paper discusses some of the properties of the deposits from these processes.

Non-metal Electroless Nickel
Organic and inorganic materials that have low hazard characteristics are available that can stabilize and brighten electroless nickel processes. Some of these materials have been used for many years in conjunction with traditional metal stabilizers and some new materials have been discovered to perform these roles. The R&D work with these materials has resulted in a class of processes that perform similarly to traditional electroless nickel but have no metals contained other than those that can be found naturally in the raw materials.

While the processes that have been developed in response to the new regulations are essentially free of lead and cadmium, careful analysis of the electroless nickel deposits will reveal the presence of some of these and other metals. In a previous paper (2) we described the sources of lead and cadmium in the best available raw materials. The typical analysis for metal (non-cadmium and non-lead) stabilized and non-metal stabilized electroless nickel deposits is about 0.0002 wt% lead and less than 0.0001 wt% cadmium. The analysis method used is important. Normal atomic absorption will likely not detect such low levels. Polarography and ICP are two methods that do have the capacity to produce reliable low level analysis.

Properties of Mid-phosphorus Non-metal Stabilize Electroless Nickel
Plating rate, percent phosphorus, deposit hardness, internal stress and deposit brightness are important properties for electroless nickel deposits. The values for these properties are presented here.

The **plating rate** of electroless processes depend strongly on the pH and temperature of the plating bath. Table I shows typical plating rates obtained for a conventional mid-phosphorus EN process (CMP) and the non-metal stabilized mid-phosphorus process (NMMP). The data in the table show that the plating rates are very similar

Table I
Plating Rates of Conventional and Non-Metal Mid-phosphorus Processes

Temperature °C	CMP pH 5.0	NMMP pH 5.0
77	11.8	14.7
82	14.5	17.0
88	19.2	21.0
93	22.8	24.9
99	26.8	25.8

Note: CMP=Conventional Mid-Phos, NMMP=Non-Metal Mid-Phos

Table II
Average wt % Phosphorus vs. Bath Age (MTO)

Bath Age MTO	CMP pH 5.0	NMMP pH 5.0
0	7.8	8.6
1	8.2	9.0
2	8.5	9.5
3	8.5	9.8
4	8.5	
5	8.9	9.7
6	9.0	9.5

The **% phosphorus** of the deposit is a critical property that determines the deposit hardness. Table II contains data that compares the NMMP deposits with conventional CMP. In this case the NMMP phosphorus content is slightly higher than the similar CMP process.

The **deposit hardness** is measured using the Knoop indenter at a 100 gram load (HK_{100}) for these deposits. Hardness is usually determined for the "as plated" deposit as well as samples that have been heat treated. Table III provides the data obtained for the CMP and NMMP deposits. The NMMP deposit hardness is slightly higher that the CMP but the % Phosphorus is also higher.

Table III
Hardness of "As Plated" and Heat Treated EN Deposits
Average HK_{100} Microhardness

Heat Treatment	CMP	NMMP
As Plated	548	566
250°C 1 hour	639	664
300°C 1 hour	873	980
350°C 1 hour	937	1045
400°C 1 hour	888	1028
450°C 1 hour	842	970

Note: CMP=Conventional Mid-Phos, NMMP=Non-Metal Mid-Phos

The **internal stress** of a deposit can be measured using several methods (5). Table IV provides some data that we have for the NMMP deposit compared with the conventional.

Table IV
Internal Stress of Deposits

Bath Age	CMP	NMMP
0 MTO	4500 PSI Compressive	2500 PSI Compressive
5 MTO	6000 PSI Compressive	5500 PSI Compressive

Note: CMP=Conventional Mid-Phos, NMMP=Non-Metal Mid-Phos

Figure 1.
Highly Stressed Compliant Electroless Nickel Deposit

The internal stress is an important issue for the compliant electroless nickel processes. Many of the materials that strongly brighten electroless nickel also greatly increase the internal stress, and it is not hard to obtain stress levels exceeding 30,000 PSI compressive. Figure 1 shows an example of a very highly stressed deposit that has been measured using commercially available stress tabs. This deposit is fairly bright for a non-cadmium process but the stress is extremely high. This high compressive stress will cause cracking in moderately high thickness deposits. The deposit shown in Figure 1 is a competitive process that can be used practically only for very thin deposits but the deposits are very bright. We have worked to provide the brightest deposits but with the lowest stress. Work on this aspect continues.

Brightness is a special issue with the compliant deposits. It is a bit of a challenge to obtain the level of brightness that cadmium provides. Brightness can be measured using a gloss meter (6,7). Table IV provides a comparison of gloss measurements at a specular angle of 20° for the conventional CMP deposits, a metal stabilized ELV compliant mid-phosphorus ELVMP deposits, and the non-metal stabilized NMMP deposits. The measurements were conducted using two different panels. The ACT GM42E (8) is a polished panel used for a special project long ago. No panel seems to be available today that has a similar polish. The ACT CRS (8) is an unpolished cold rolled steel panel that is currently available. The gloss measurement is strongly affected by the base metal but the gloss measurement ranks are comparable. These measurements represent the brightness levels that are currently attainable while keeping the stress at acceptable levels.

Table V
Brightness of Electroless Nickel Deposits

Deposit	Gloss ACT GM42E	Gloss ACT CRS
Conventional CMP	809GU	265GU
ELV Compliant ELVMP	581GU	153GU
Non-metal NMMP	340GU	104GU
Bare Steel Panel	187GU	77GU

Note: CMP=Conventional Mid-Phos, NMMP=Non-Metal Mid-Phos

Product Configuration of the Non-Metal Stabilized Electroless Nickel

One of the constraints in the design of electroless nickel products is that some components are not easily mixed with others. As an example, it is usually not possible with conventional processes to mix lead compounds with concentrated liquid nickel sulfate (LNS) because the compound lead sulfate is insoluble. By the time the customer needs to use the product this important stabilizer will not longer be in solution. Similar problems present themselves to the formulator of compliant processes because some of the materials will not stay in solution or may be deactivated. Thus we sometimes see processes that have four components rather than the normal three components, or some components might be more dilute than normal.

The non-metal stabilized process can be formulated with is several ways. When cost cutting issues become important, customers look to save costs by using liquid nickel sulfate (LNS). The used of LNS has its disadvantages. This highly concentrated material is naturally unstable and the nickel sulfate will crystallize in the bottom of the container in time or during cool weather. However, if used quickly and kept warm these problems are minimized. On the plus side, the

LNS available is usually the highest purity available and the use in a plating shop tends to be much more economical. The use of non-metal stabilizers makes it easier to produce a process that can use LNS. It is also easier to provide a process that can be added at a 1 to 1 ratio with the LNS. LNS contains about 135 g/L of nickel metal ions and thus is usually used at 45% by volume in a typical plating bath to obtain 6 g/L nickel. A process that is used at a 1 to 1 ratio with LNS must be considerably more concentrated than the normal 5% or 6% by volume processes. It has been found that it is fairly easy to provide a process that is considerably more concentrated. Table VI shows the make-up and maintenance parameters for the conventional processes compared with what is possible for the non-metal process

Table VI
Possible EN Non-Metal Maintenance Products

EN Product	Conventional CMP	Non-metal NMMP	Non-Metal Two Part
Nickel Component	6 vol %	4.5 vol % LNS	Not used.
Makeup Reducer	15 vol %	9.0 vol %	15 vol % All-in-One
Maintenance Reducer	6 vol %	4.5 vol %	10 vol % All-in One

At the same time, it is possible to formulate a two part process (Table VI) in which one component is used for make-up and one component is used for maintenance. This configuration provides for a much simpler operation at tank-side. For the Two Part configuration the only limitation is the ability to formulate nickel and sodium hypophosphite in the same container.

Properties of High-phosphorus Non-metal Stabilized Electroless Nickel

The mid-phosphorus NMMP process is well developed, but there is a market for non-metal stabilized high-phosphorus processes as well. The high-phosphorus process, NMHP, is in development and shows considerable promise. Table VII shows the desired properties of the NMHP process and the level of achievement at the time of this writing. The high-phosphorus process is a work in progress and progress will be reported in the future.

Table VII
Properties of Non-Metal High-phosphorus Electroless Nickel

High Phos. Property	Desired Value	Achievement
Plating Rate	10-12 um/hour	Achieved
Internal Stress	-2000-0 PSI Tensile	Achieved
Hardness As Plated	500-600 HK100	Not Measured
Hardness Best Hardness	850-900 HK100	Not Measured
Nitric Acid Test (100%)	No Darkening for 1 min.	Achieved

Summary

1. The high-phosphorus process is under development. Deposit properties determined at this writing are similar to deposits obtained from some conventional high-phosphorus processes.

2. The plating rate, deposit phosphorus content, hardness and internal stress of deposits plated from the non-metal stabilized mid-phosphorus process have been reported here and are all very similar to conventional processes.

3. The brightness or gloss of non-lead and non-cadmium processes is less than that achieved by cadmium brightened processes at this time. The brightness of the non-metal stabilized processes is a bit less at this writing.

4. The improvement of deposit brightness is complicated by the fact that most brighteners have strong adverse affects on deposit stress.

5. The non-metal stabilized processes have fewer formulation constraints compared with both conventional and ELV compliant processes. Thus, it is easier to formulate unusual addition components.

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