Lead and Cadmium Free Electroless Nickel Processes For The 21st Century

David E. Crotty, Ph.D., MacDermid, Inc. New Hudson, MI

Specifications are increasingly requiring lead and cadmium free electroless nickel coatings for applications as diverse as automotive, electronic and food handling equipment. This paper discusses the properties of a wide range of electroless nickel and electroless nickel/PTFE deposits that are designed to meet these needs. As for traditional electroless nickel deposits, the properties of these new deposits are strongly influenced by the phosphorous content of the deposit.

For further information contact:
David Crotty, Ph.D.
MacDermid, Inc.
29111 Milford Rd.
New Hudson, MI 48165
Phone: 248.437.8161
FAX. 248.437.1560
dcrotty@macdermid.com

Introduction

Electroless plating processes are unusual because they do not use current to drive the deposition of metals, a reduction process. The electroless processes use chemical reducing agents to perform the deposition. The difficulty is that the process has an oxidizing agent (the metal) and a reducing agent (sodium hypophosphite in many cases) in the same solution and the result can be a spontaneous reduction of all the metal in the process container. In the early days of electroless nickel plating the inventors observed that the bath was stable sometimes but unstable other times. Eventually it was discovered that the source of nickel often had other metal impurities and these metals, if present in sufficient quantity, would stabilize the operation of the plating bath. Two of the metals that were found to stabilize electroless nickel were lead and cadmium. The lead acted like a "poison" to the process, preventing the nickel from initiating on the walls of the glass, plastic or stainless steel containers. Cadmium also helped as a stabilizer but primarily served to brighten the nickel deposit. Subsequently, virtually all electroless nickel processes used very small amounts of lead and some used cadmium for the brightener.

Lead and cadmium salts and metals are, of course, hazardous to humans in particular and to the environment in general and we are aware of the very serious consequences when leaded paint is ingested by infants or if cadmium gets into the food chain. With an increasing emphasis on recycle-ablity, governments around the world became aware of these hazards and began to write regulations concerning the removal of these and other materials from products. Even though the lead and cadmium in electroless nickel deposits are in very low concentrations and generally considered non-hazardous even for some food processing applications, these deposits became subjected to the scope of the regulations.

In the United States the Food and Drug Administration (FDA) has given NSF International, a non-profit and non-government organization, the authority to publish regulations concerning a wide range of safely issues. As part of this effort NSF International published NSF/ANSI 51-2002 Food Equipment Materials [1]. In this regulation sections 4.1.2 and 4.1.3 read:

2.2.2 Food zone materials shall not contain lead, arsenic, cadmium, or mercury as ***intentional ingredients*** (emphasis added by author), except where brass and bronze are specifically permitted for use under section 4.2.3.2.

2.2.3 Coatings containing lead as an intentional ingredient shall not be used on food equipment surfaces including splash zones and non-food zones. Coatings with an unintentional lead content (lead impurity) greater than 0.06% shall not be used.

Lead and cadmium used by EN formulations result in quantities of less than 0.06% w/w in their nickel deposits, but they are clearly "intentional ingredients" and thus are restricted by the regulation. These regulations have been in effect since 2002.

The European Union has also addressed these issues. In the effort to provide safe and complete recycleability the EC has developed the End of Life Vehicle (ELV) Directive 2000/53/EC Annex II [2]. As part of that effort ELV directive 2000/53/EC Annex II June 2002 [2] reads

> "Notes:
> - a maximum concentration value up to 0,1 % by weight and per homogeneous material, for lead, hexavalent chromium and mercury and up to 0,01 % by weight per homogeneous material for cadmium shall be tolerated, provided these substances are not ***intentionally introduced*** (1) " (emphasis added by author).
>
> and goes on to read:
>
> (1) "Intentionally introduced" shall mean "deliberately utilized in the formulation of a material or component where its continued presence is desired in the final product to provide a specific characteristic, appearance or quality".

General Motors, Ford, Chrysler and other global OEMs have developed standards that follow these guidelines for equipment that is assembled into automobiles that are intended to be sold in Europe. While currently the regulations only apply to Europe, the American market recognizes the need to be able to sell freely in the European market as it is not practical to have separate products for each market.

In addition to the European automobile market, there is a movement in the electronics market to remove hazardous heavy metals to facilitate recycling. The Waste Electrical Electronic Equipment (WEEE) Directive 2002/96/EC targets electronic equipment. Further, the Restrictions of Hazardous Substances (RoHS) Directive 202/95/EC [3] requires:

> Article 4.1 – Prevention
>
> "Member States shall ensure that, from 1 July 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE). National measures restricting or prohibiting the use of these substances in electrical and electronic equipment which were adopted in line with Community legislation before the adoption of this Directive may be maintained until 1 July 2006.

The phrase "intentionally introduced", is not found in the WEEE or RoHS documents. However there are many published discussions between the EC and manufacturers that do use this phrase with respect to the availability of substitutes for the targeted items. The implication is that the phrase "intentionally introduced" is significant and this phase has been added to many electronic and other OEM specifications. Table I lists the six targeted substances in RoHS.

Table I
RoHS Substance Proposed Maximum

Substance	Proposed Maximum Concentration
Lead	0.1% w/w
Mercury	0.1% w/w
Cadmium	0.01% w/w
Hexavalent Chromium	0.1% w/w
Polybrominated Biphenyls PBB	0.1% w/w
Polybrominated diphenyl ethers PBDE	0.1% w/w

While the strongest effect of these directives is on soldering processes (although there are some exemptions), they also apply to any item that goes into electronic equipment. These regulations go into effect in July 2006, but parts manufacturers do not want to redesign equipment and are requiring these changes now.

In Japan the "Green Procurement Policies" of leading electronics companies such as Sony, Matsushita, Canon, etc. is leading to the elimination of these types of materials as well from electronics equipment. Japanese companies have put these policies into effect as of April 2005.

While it is possible to use certain non-toxic or low-toxicity metals as stabilizers for electroless nickel, some Japanese electronic companies are also specifying electroless nickel deposits with no metal stabilizers at all.

The electroless nickel market has responded to these regulations with a full range of processes to meet the needs of equipment manufacturers. This paper discusses the properties of the deposits from these new processes and compares these properties with conventional deposits.

Electroless nickel deposits

Sources of Lead and Cadmium. Electroless nickel deposits are classified by the phosphorous content in the deposit because it has been shown [4,5] that the properties of electroless nickel vary with phosphorous content. The proper choice of the phosphorous range must be determined by the application's requirements. High phosphorous is usually above 10% P, medium phosphorous is usually considered 7-9% P and low-medium phosphorous is considered to be 4-6% P.

Typical conventional high phosphorous deposits contain 0.025 to 0.035 weight % of lead but cadmium is seldom added to this type of process. Conventional medium phosphorous electroless nickel deposits contain about 0.050 to 0.065 weight % of lead and 0.050 to 0.12 weight % of cadmium.

The development of lead and cadmium free electroless nickel deposits must face the problem that some lead and cadmium is present as trace impurities in the raw materials. For example, early sources of nickel metals and salts used to make nickel sulfate concentrates and salts sometimes had enough trace impurities of lead and other metals to prepare a reasonably stable plating bath without an intentional addition of these metals. Today, the liquid nickel sulfate concentrates are usually made with nickel carbonyl, which is very clean. Our experience is that the liquid nickel sulfate contains less than 0.0001 g/L. If a liquid nickel sulfate concentrate (135 g/L Ni ions) is used at 4.5% v/v to make a typical electroless nickel bath of 6 g/L of nickel metal then the amount of lead that enters the plating bath would be equal to 0.045x0.0001 = 0.0000045 g/L.

The sodium hypophosphite is another source of trace heavy metals contamination. Most sources of sodium hypophosphite provide specifications that quote a maximum of heavy metals (analyzed as lead) to be under about 1.0 PPM or 0.000001 g/g of hypophosphite. A typical EN plating bath is generally formulated with 30 g/L of sodium hypophosphite, thus adding about 0.000030 g/L to the plating bath. Given these amounts, the total from nickel and hypophosphite could be about 0.0000345 g/L. If all of this lead is deposited with the 6gm/L nickel in a typical EN plating bath this translates to about 0.00058 weight %.

Thus, it is possible, with impure nickel and hypophosphite sources, to obtain an electroless nickel deposit with measurable levels of lead and cadmium, even though no lead or cadmium compounds were added intentionally to the formulation. Fortunately, there are a few sources of nickel and hypophosphite that contain less than the amounts that are quoted here as maximums. In our work the formulated non-lead and not-cadmium medium phosphorous deposits have been analyzed to contain 0.00027 weight % lead and 0.0001 weight % of cadmium. Similarly the non-lead high phosphorous deposits have been found to contain 0.00023 weight % lead and <0.00007 weight % cadmium (the detection limit for ICP analysis). These amounts of lead and cadmium result in the formulation from raw materials despite the fact that the materials chosen are the highest purity available in the market.

Some specifications require less than 0.0002 weight % of lead or cadmium in the deposits. There will be difficulty meeting this level, especially if the best worldwide commercial sources of raw materials will not meet this requirement. Better sources must be found to meet these specifications for lead. Such a specification for cadmium can be met with conventional best sources.

Table II is a listing of the general characteristics of a selected group of processes and deposits that we will discuss in the following pages.

Table II
General Characteristics of Selected Plating Processes

Process	Process Type	Brightness (5=brightest)	Plating Rate (um/hr)	Thickness Build-up
787Conv	Medium Phos with Pb/Cd	5.0	14-22	High Build
1000Conv	High Phos with Pb	3.0	4-6	High Build
101Conv	High Phos with Pb	3.0	4-12	High Build
4200Conv	High Phos with Pb	3.0	4-12	High Build
805NLC	Low Phos w/o Pb/Cd	4.0	4-6	Medium Build
807NLC	Medium Phos w/o Pb/Cd	3.5	10-18	High Build
809NLC	Medium Phos w/o Pb/Cd	4.5	14-22	Medium Build
811NLC	High Phos w/o Pb/Cd	4.0	10-15	High Build
EX-NM	Medium Phos w/o metals	4.5	14-25	High Build

Note: NLC=Non-Lead/Cadmium; Conv=Conventional; EX-NM= Experimental Non-Metal

Properties of Non-Lead/Cadmium Deposits

The properties of electroless nickel deposits that differentiate the various processes include plating rate, % phosphorous, and deposit hardness. The enclosed tables provide some of the data collected.

Plating Rate. Table III lists the plating rate data for several processes under typical operating conditions for each type. Those processes designated as NLC are non-lead/cadmium processes. Table III provides data for four medium phosphorous processes: two non-lead/cadmium processes (807NLC and 809NLC) one conventional lead/cadmium process (787Conv) and one experimental non-metal process (EX-NM). Table III also provides the rate data for three high phosphorous processes: one non-lead/cadmium (811NLC) and two conventional processes (1000Conv and 4200Conv). Figures 1 and 2 illustrate this data a bit further. The comparative data presented show that the various processes have slightly different rate performance but the medium-phosphorous processes are faster plating than the high-phosphorous processes. The table also makes it clear that the non-lead/cadmium processes operate very similarly when compared with the conventional processes.

The medium phosphorous processes in Table III are 807NLC, 809NLC, 787Conv and EX-NM. The 809NLC is very similar to the 787Conv in terms of plating rate. The 807NLC has a slower rate but is designed to prepare high build deposits. The EX-NM has a slightly faster rate and is capable of high build deposits.

The high phosphorous processes in Table III are 811NLC, 1000Conv and 4200Conv. These 811NLC and 4200Conv are similar in rate. The 1000Conv is slower but was designed to prepare a very highly corrosion resistance deposit and had been used to plate computer memory disks that require very high % phosphorous and thus a lower plating rate.

Table III
Average Plating Rates (um/hr) Vs Temperature

Temp °C	807NLC pH 5.0	809NLC pH 5.0	787Conv pH 5.0	EX-NM pH 5.0	811NLC pH4.8	1000Con pH 4.8	4200Con pH 4.8
77	8.8	10.2	11.8	14.7	8.8	5.0	8.7
82	10.6	13.6	14.5	17.0	10.6	7.6	10.4
88	14.7	17.8	19.2	21.0	14.6	10.1	14.6
93	16.9	21.3	22.8	24.9	15.2	12.7	15.6
99	18.5	26.0	26.8	25.8	15.8	14.8	16.2

Note: NLC=Non-Lead/Cadmium; Conv=Conventional; EX-NM= Experimental Non-Metal

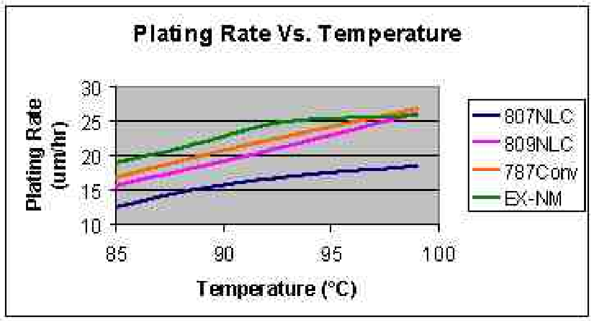


Figure 1 Plating Rate Vs. Temperature, Mid Phosphorous Processes

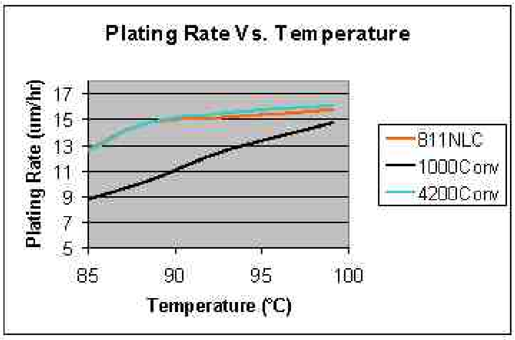


Figure 2 Plating Rage Vs. TemperatureHigh Phosphorous Processes

Phosphorous Content. Table IV lists the average % Phosphorous (w/w) vs. Bath Age for many of the same processes. Figure 3 provides a graphic plot of this data. The medium-phosphorous processes show a slight tendency to increase phosphorous content with bath age, perhaps because the plating rate slows slightly as the bath ages. We can see that the medium phosphorous processes differ slightly. The two high-phosphorous processes are very similar in this regard.

Table IV
Average % Phosphorous (w/w) vs. Bath Age (MTO)

MTO	807NLC pH 5.0	809NLC pH 5.0	787Conv pH 5.0	EX-NM pH 5.0	811NLC pH 4.8	4200Conv pH 4.8
0	8.5	8.0	7.8	8.6	10.8	10.6
1	8.8	8.2	8.2			10.9
2	8.9	8.4	8.5		11.0	10.9
3	9.0	8.5	8.5	9.8		11.0
4	9.1	8.5	8.5		11.4	11.3
5	9.2	8.7	8.9	9.7		11.2
6	9.3	8.8	9.0		11.6	11.3

Note: NLC=Non-Lead/Cadmium; Conv=Conventional; EX-NM= Experimental Non-Metal

Figure 3
Plating Rates vs. Bath Age

Table V
Average % Phosphorous (w/w) vs. Temperature

Temperature (°C)	807NLC pH 5.0	809NLC pH 5.0	787Conv pH 5.0
77	9.4	8.9	9.1
82	8.9	8.5	8.6
88	8.6	8.1	7.9
93	8.2	7.7	7.5
99	7.9	7.4	7.0

Table V provides another view to compare several medium-phosphorous processes in terms of % phosphorous (w/w) vs. temperature. The processes are very similar but slight differences can be seen.

The conventional and NCL counterparts for both the medium phosphorous and high phosphorous processes are essentially similar in terms of phosphorous content.

Deposit Microhardness. The deposit hardness, reported as an average, is an important indication of wearability. In general the hardness has been measured as HK_{100} (Knoop at 100 gram load) and the results are presented for "as plated" deposits and heated to a range of temperatures from 250°C to 450°C for one hour. Table VI lists the hardness values for some of the electroless nickel deposits.

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

Heat Treatment	805 NLC	787 Conv	807 NLC	EX-NM	809 NLC	4200 Conv	811 NLC
As Plated	540	548	520	566	540	503	515
250°C	-	639	627		653	566	589
300°C	-	873	855		883	864	875
350°C	-	937	907		945	917	927
400°C	890	888	865		899	906	888
450°C	-	842	827		825	862	827

Notes: a. Heat treatments are generally one hour, b. The EX-NM is experimental and parameters may change.

The hardness values in Table VI show that for conventional and NLC processes the deposits can be heat treated to best hardness at about 350°C for one hour, as found in previous reports [4].

Taber Wear Performance. Electroless nickel deposits are often tested for wear using the Taber Abraser Wear test [4,5,6] and the results usually (but not always) follow with the hardness. Table VII lists the Taber Wear results for a range of processes deposits. In Table VII the Taber test is conducted on the deposit in "as plated" condition and at best hardness. We can see from Table VI that the best hardness for electroless nickel deposits is usually obtained with a one-hour heat treatment at about 350°C.

The Taber Abraser data presented in Table VII is a representative grouping of data taken from a more complete study in progress. A complete report will be published in the near future.

Table VII
Taber Abraser Wear Comparisons
Average Taber Wear Index (mg loss/1000 cycles)

Process	As Plated	Heat Treated 350°C 2 hours
805NCL	13.5	8.7
809NCL	18.9	10.0
811NCL	19.8	11.6
5000Conv	17.6	9.9
LowP Conv [4]	9.1	9.9
MidP Conv [4]	19.6	10.3
HighP Conv [4]	24.1	14.1

Note: Reliable results are only obtained if the abraser wheel is dressed every 1000 cycles. These results are the average of 9 or 10 runs of 1000 cycles.

Corrosion Protection. Another very important property of electroless nickel deposits is corrosion protection. Table VIII collects the neutral salt spray performance results for a range of deposits during ASTM B117 [7] neutral salt spray testing.

Table VIII
Neutral Salt Spray ASTM B117
Typical Hours to First Corrosion for 25 um Plate Thickness
Red Corrosion for Steel, White Corrosion for Aluminum

EN Process	Aluminum Substrate	Steel Substrate
807NCL	>48 hrs	>96 hrs
809NCL	>48hrs	>96hrs
787Conv	>48 hrs	>96hrs
811NCL	240-750 hrs	240-750 hrs
4200Conv	240-750 hrs	240-750 hrs

Again, the NCL processes have corrosion protection properties that are very similar to the conventional processes.

Properties of Electroless Nickel/PTFE Deposits

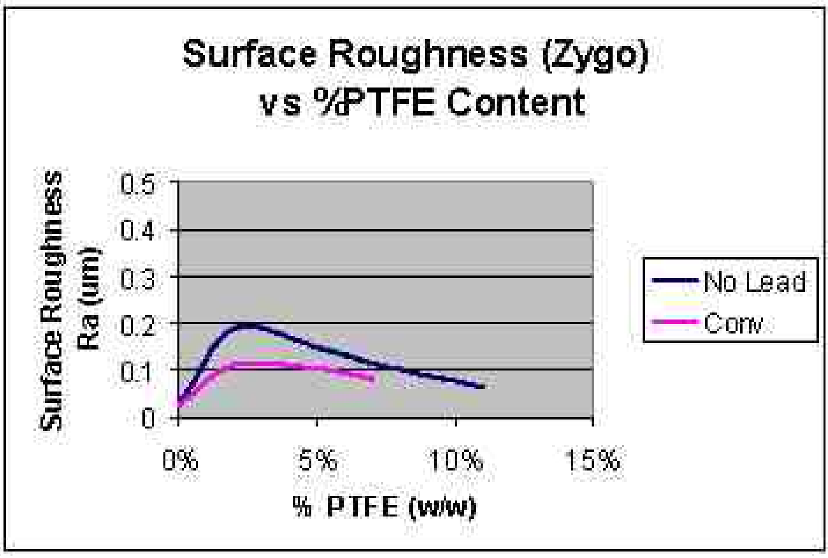
Electroless nickel deposits can be prepared with particulate co-deposits, and diamonds, boron nitride, silicon carbide [8] and PTFE [9] are particles that are commonly used in this way. The friction and wear properties of EN/PTFE deposits have been investigated extensively in the past and were reviewed [10] recently. The EN/PTFE deposits are used in food and medical equipment where they come under the NSF/ANSI 51 [1] regulations and they are used in automotive and electronic applications where the ELV [2] and WEE [3] directives apply. In response to these regulations an electroless nickel process has been developed that is lead and cadmium free. This electroless process is compatible with existing PTFE dispersions.

Surface Roughness. Table IX shows the comparison between the conventional and non-lead deposits in terms of plating rate and average surface roughness, Ra. Both sets of data were obtained using the same PTFE dispersion [9]. The surface roughness was measured using the Zygo optical profileometer and the Taylor Hobson Surtronic 3P mechanical profileometer. Figure 4 provides a plot of the data from the Zygo profileometer.

Table IX
Deposit % PTFE Vs Average Surface Roughness, Ra and Plating Rate
Comparisons of Conventional and Non-Lead Processes

%PTFE (wt/wt)	Plating Rate (um/hr)	Surface Roughness Ra (um) Zygo	Surface Roughness Ra (um) Taylor Hobson
Lead Free Process			
0%		0.027	0.05
2%	13	0.188	0.29
5%	5	0.147	0.25
7%	8	0.115	0.16
11%	4	0.062	0.18
Conventional			
0%		0.025	0.05
2%	6	0.112	0.19
4%	7	0.105	0.27
7%	9	0.080	0.16
Bare Steel			0.02

Figure 4
Surface Roughness Ra (Zygo) Vs. Deposit % PTFE



Friction Properties. The wear properties of EN/PTFE deposits were investigated recently [10] with an older friction and wear test instrument to compare the wear properties of deposits prepared with new and traditional PTFE dispersions. That investigation provided useful information but the instrumentation was not sensitive enough to truly measure the coefficient of friction of the deposits. Because of this we continued this investigation by using more sensitive Micro Photonics Nano Scratch Tester (NST) [11]. The NST test consists of loading an indenter tipped with a 6 mm diameter chrome-steel ball. The indenter is loaded to 25mN (about 2.6 grams) and drawn across the surface of the deposit at a speed of 3 mm/min for a distance of 3 mm. The test is conducted three times using the same ball 1 mm away from the last test on the surface and the average coefficient of friction for each test is calculated. The results of these tests are shown in Table X and Figure 5.

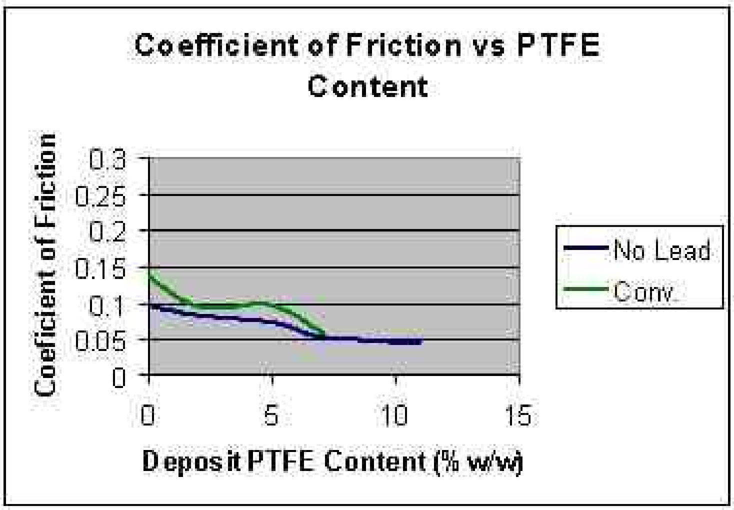
The deposits shown in Table X were prepared on very smooth panels normally used for Hull cell work (see Table IX). The table shows the coefficient of friction for the bare steel, the conventional electroless nickel without PTFE, the non-Lead/Cadmium electroless nickel without PTFE as well as the deposits with a range of PTFE content. In this work we were aware that the PTFE could contaminate an indenter ball and this would influence following results. For this reason the technician used a fresh ball on the indenter for each three run test.

Table X
Nano Scratch Tests of EN/PTFE deposits plated from Conventional and Non-Lead Processes
Coefficient of Friction (u) measured three times

Deposit %PTFE w/w	CoF Run 1	CoF Run 2	CoF Run 3	CoF Average of 3	CoF Average of 2
Bare Steel	0.376	0.370	0.410	0.385	
Conv 0%	0.200	0.137	0.136	0.158	0.137
Conv 2%	0.215	0.102	0.088	0.135	0.095
Conv 4%	0.222	0.095	0.101	0.139	0.098
Conv 7%	0.151	0.057	0.064	0.139	0.061
NLC 0%	0.115	0.097	0.095	0.102	0.096
NLC 2%	0.186	0.097	0.070	0.117	0.084
NLC 5%	0.227	0.090	0.059	0.125	0.075
NLC 7%	0.073	0.054	0.050	0.059	0.052
NLC 11%	0.108	0.046	0.041	0.065	0.044

Note: Conv=Conventional with Lead/Cadmium, NLC=Non-Lead/Cadmium

Figure 5
Coefficient of Friction Vs. Deposit PTFE Content



It is interesting to note that the first scratch of the EN deposits and the PTFE containing deposits exhibits a much higher coefficient of friction than the second and third scratches. It seems possible that the first scratch smoothes the surface of the indenter ball or picks up some PTFE to lubricate the next two runs. In any case the measurement provides a lower coefficient of friction after a very short period of movement. It seems possible that the second two measurements are more significant for a surface that sees continuous use. As with normal electroless nickel deposits, the NLC and the conventional processes provide deposits with very similar properties.

Summary and Conclusions

- The movement to develop electroless nickel processes that do not contain "intentionally added" lead and cadmium has been driven by directives from governmental and industrial bodies. Three of the directives from the European Union, designated as ELV, WEEE and RoHS, are discussed as well as the "Green Procurement Policies" of Asian electronics manufacturers. These directives, for the most part, insist that lead and cadmium (amongst other materials) must not be added intentionally to the processes.
- The most important point of this comparison is that the first generation non-lead and non-cadmium deposits have properties that are very similar to their conventional counterparts. Many conventional cadmium brightened mid phos systems produce an extremely bright deposit at the beginning of the solution life, but this tends to become less bright after the third metal turnover. The first generation NLC systems are bright deposits but more importantly provide more consistent brightness over the entire range of bath life in direct comparison to cadmium brightened deposits. On the other hand, the non-lead and non-cadmium high phosphorus process produces a brighter deposit than the conventional high phosphorus system. The visual appearance of NLC electroless nickel/PTFE composites are also very similar to their conventional counterparts.
- The plating rates of conventional and NLC (non-lead and cadmium) processes are compared and found to be very similar.
- The deposit phosphorous content of the conventional and NLC processes are compared and found to be very similar.
- Hardness values, measured as Knoop at 100 gram load, are shown to be similar for the conventional and NLC processes. As with previous work, electroless nickel deposits can be treated to best hardness at about 350°C for 1 hour.
- Taber Abraser wear test results are reported from previous work and from a testing program in progress. The results show that deposits from conventional processes perform similarly with those from NLC processes.
- Corrosion protection, as determined by ASTM B117 neutral salt spray tests, is identical with the conventional deposits and the NCL deposits.
- Electroless nickel/PTFE composites are also subject to the directives. The surface roughness and coefficient of friction properties of conventional and NLC deposits are reported and shown to be similar.

Acknowledgements

The author would like to acknowledge efforts of Ken Bagnall, Brad Durkin, Ed Komarnicke, Mike Malik, and Carl Steinecker, all of MacDermid, Inc., in the collection of the data presented here and for helpful discussions during the preparation of this paper.

References

1. NSF/ANSI 51-2002 Food Equipment Materials, NSF International, Ann Arbor, MI, (2002).
2. End of Life Vehicle (ELV) Directive 2000/53/EC Annex II June 2002, http://europa.eu.int/eur-lex/
3. Waste Electrical Electronic Equipment (WEE) Directive 2002/96/EC and Restriction of Hazardous Substances (RoHS) 2002/95/EC, http://europa.eu.int/eur-lex/.
4. L. Weisenberger, J. Greene, Proc. EN Conference 1988, Products Finishing, Cincinnati Ohio (1988).
5. B. Durkin, D. Crotty, Proc. AESF SUR/FIN92 (1992).
6. Test Method B733 Appendix X1, ASTM, Philadelphia, PA.
7. Test Method B117, ASTM, Philadelphia, PA.
8. Niklad Dispersant TDS, MacDermid, Inc., Waterbury, CT.
9. Niklad ICE TDS, MacDermid, Inc., Waterbury, CT.
10. D. Crotty, Proc. AESF SUR/FIN2004 (2004).
11. Microphonics Nano Scratch Tester, Micro Photonics, Inc., Irvine, CA.