ELV-Compliant Speciality Electroless Nickel Processes

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Over the past few years numerous papers have been given on ELV compliant electroless nickel solutions. This paper is going to discuss two specialty electroless nickel processes, Ni-PTFE and Black EN.

Electroless nickel/PTFE deposits provide a homogeneous coating with a low coefficient of friction for dry lubrication applications. Deposit properties such as rate, hardness, and PTFE content will be discussed, both in current and ELV-compliant processes, outlining the benefits of current technology and the improvements made with an ELV-compliant process.

A new black electroless nickel process that has good hardness and color will be described in this paper and compared to previous published black electroless nickel process. This new process also does not use nitric acid as the blacking solution.

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Electroless Nickel/PTFE: Current and ELV-Compliant Technologies

Introduction

Electroless nickel deposits offer many distinct advantages over other processes where wear and corrosion resistance are critical. This type of deposit also provides the advantage of uniform coverage on the work, whereas deposit thickness often varies with electrolytic processes. Because of these advantages, electroless nickel deposits are specified for many applications.

A subsection of electroless nickel plating is composite coatings. Several materials are commercially available for codeposition for a Ni-P-X matrix, including diamonds, silicon carbide, and polytetrafluoroethylene (PTFE), for example; each with their own unique attributes which meet specific wear and frictional requirements.

The goal of a Ni-P-PTFE deposit is to provide the benefits that both materials provide: the wear resistance and hardness of electroless nickel, and the low coefficient of friction that PTFE provides. The matrix results in a self-lubricating deposit with a low coefficient of friction; one that is wear resistant, relatively hard, and corrosion resistant as well.

With legislation requiring more environmentally friendly processes, a need was created for new Ni-P-PTFE technology that can meet these new requirements as well as provide improved performance over current technology. A new ELV process was developed which provides a higher deposition rate, longer bath life, and higher bath stability as well.

Method of Codeposition

One of several ways to create a composite matrix, with or without applied current, is to suspend the desired material in the plating bath and supply a mechanism for the material to be incorporated into the deposit. Bath circulation, stirring, and air agitation are three mechanical methods to suspend particles.[1]

Particles can be suspended chemically by imposing an electrical charge as well. With the use of ionic and nonionic surfactants, a charge can be imposed upon PTFE particles so that the material can be kept in suspension. This also provides a mechanism by which the PTFE can be incorporated into the deposit. In the case of Ni-P-PTFE, surfactants can be used to suspend PTFE particles within a bath, each having a positive charge. This method helps to prevent agglomeration of the PTFE due to each particle having the same charge and also repels the particles from aqueous nickel. Figure 1 (below) provides an illustration of PTFE suspended in an electroless nickel bath:

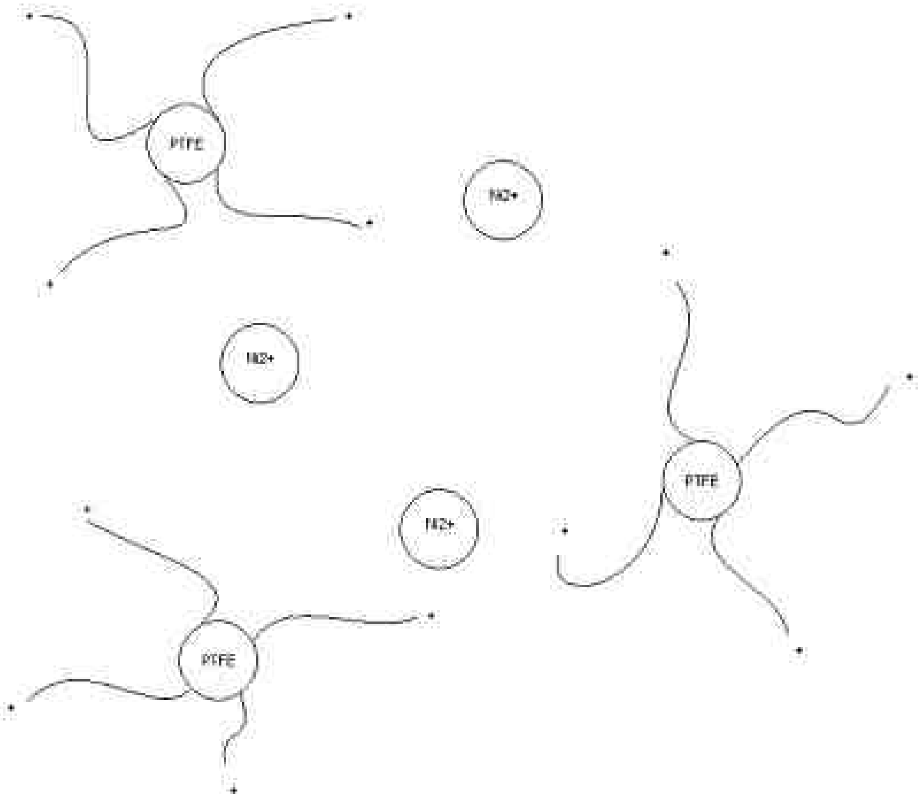

Figure 1: Suspension of PTFE particles for Ni-P-PTFE plating

Typically a PTFE dispersion concentrate is made using fine PTFE particulate and a blend of predetermined surfactants and other additives. It is from this concentrate that the PTFE is added to the electroless nickel bath. The plating bath must be mixed well prior to processing to ensure the PTFE is properly dispersed.

Bath agitation and filtration are important to maintaining the plating solution and prolonging bath life. PTFE has a density much greater than that of water (2.2 g/cm^3), and thus it has a natural tendency to gravitate to the bottom in an aqueous environment over time. PTFE particles, to maintain their suspension, are typically submicron in size. Regular bath agitation, even while no work is being processed, is key to maintaining the PTFE suspension within the bath. Bath filtration through a coarse membrane is also important, as it removes agglomerated material but allows the active PTFE to remain in the bath. If agglomerated PTFE is not removed, it can cause poor deposit quality in the form of deposit roughness.

A Ni-P-PTFE plating solution is typically made by adding a PTFE dispersion to a specific electroless nickel plating bath. The PTFE, along with the nickel and phosphorus, is positively charged, thus attracted to the work and codeposited. The desired level of PTFE incorporation into the Ni-P-PTFE matrix of course depends on the level of PTFE dispersion that is added. For many applications, 20% v/v of PTFE is acceptable. More than 30% v/v PTFE in the matrix results in the deposit losing cohesion and thus becomes undesirable.

Cross Section

Ni-P-PTFE deposits, with homogenous distribution of PTFE within the matrix and proper level of PTFE incorporation, provide a surface that maintains its properties throughout the life of the deposit. Figure 2 (below) provides a magnified cross section of a Ni-P-PTFE deposit. Figure 2 (page 5) shows the homogeneity of the deposit by elemental x-ray analysis; nickel, phosphorus, and PTFE are color coded to better illustrate distribution within the matrix.

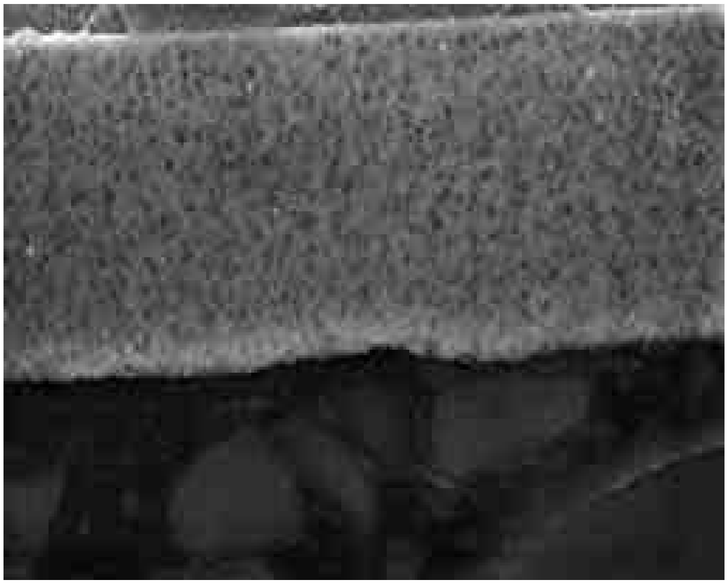

Figure 2: Cross-section of Ni-P-PTFE at 10,000X, 24% v/v PTFE

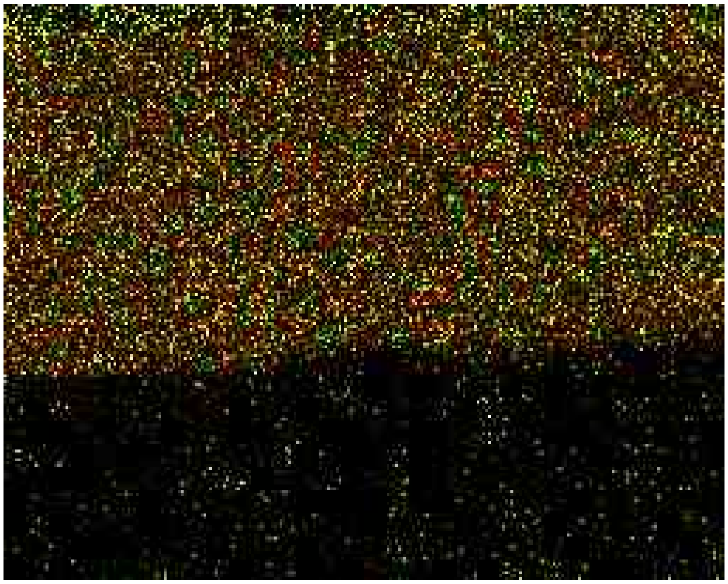

Figure 3: Cross section from Figure 1 with elemental x-ray mapping analysis (Nickel = Red, Phosphorus = Green, PTFE = Yellow)

Hardness

One of the benefits of an electroless nickel deposit is its hardness, and is maintained even when a soft material such as PTFE is incorporated. Hardness values of typical electroless nickel deposits and Ni-P-PTFE composites, all heat treated at 300°C for 1 hour, can be viewed in Table 1[2]:

Deposit	**Hardness (HK_{100})**
Low-P EN	750
Mid-P EN	550
High-P EN	500
Ni-P-PTFE	450

Table 1: Hardness values for various electroless nickel deposits

Heat treatment of a Ni-P-PTFE deposit has many advantages. The melting point of PTFE is 325°C[3]. Heat treatment will harden the Ni-P deposit, but it will also melt the PTFE within the matrix, forming a PTFE film on the surface. This film greatly increases corrosion resistance and provides a solid film of PTFE, which can add more lubricity to the part. Too high a heat treatment temperature will begin to degrade the PTFE and a discolored deposit will result.

ELV Technology

ELV-compliant technological developments have provided a means of making Ni-P-PTFE technology more environmentally friendly while meeting recent legislative requirements. This opportunity has also allowed for process improvements, namely in the aspects of deposition rate and bath life.

With current technology, to obtain 20% v/v PTFE, the deposition rate for a PTFE composite bath is approximately 5 microns/hour at makeup when operated at recommended parameters, and the bath, if properly maintained, can operate through 2-3 metal turnovers. An ELV-compliant Ni-P-PTFE process provides a 40% higher deposition rate and lasts 3-4 metal turnovers. The bath provides a homogenous deposit and at least 20% v/v PTFE incorporation.

Figure 5 illustrates the benefits of an ELV-compliant Ni-P-PTFE process provides over current technology:

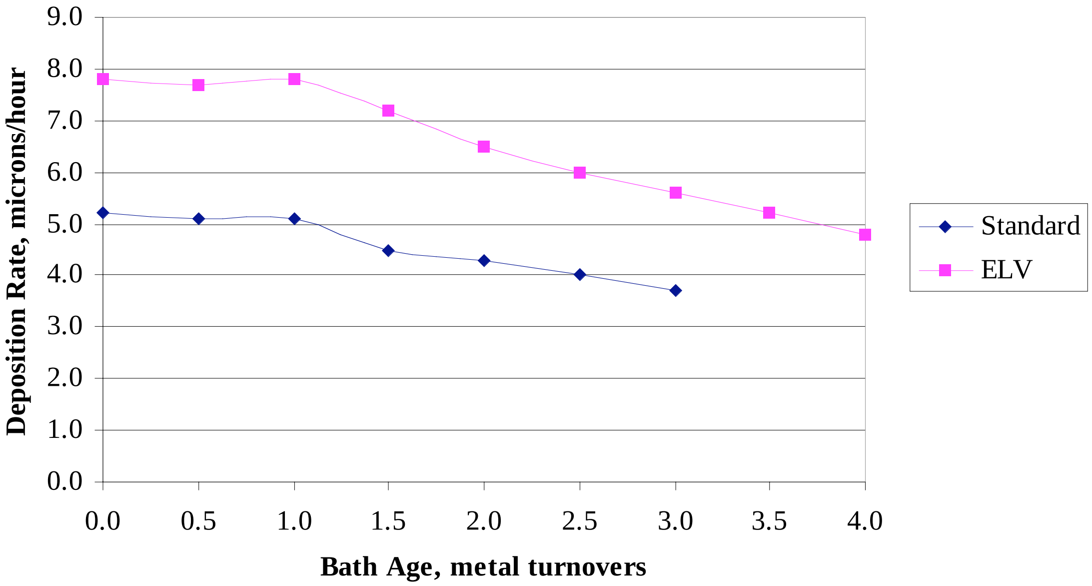

Figure 5: Comparison of ELV-compliant technology over current technology; both processes maintained to codeposit approximately 20% v/v PTFE

The impetus for the development of a more environmentally friendly process has allowed for the improvement over current technology, not just in significantly increased deposition rate, but longer bath life.

New technology has also allowed for the vast increase in bath stability (Figure 6):

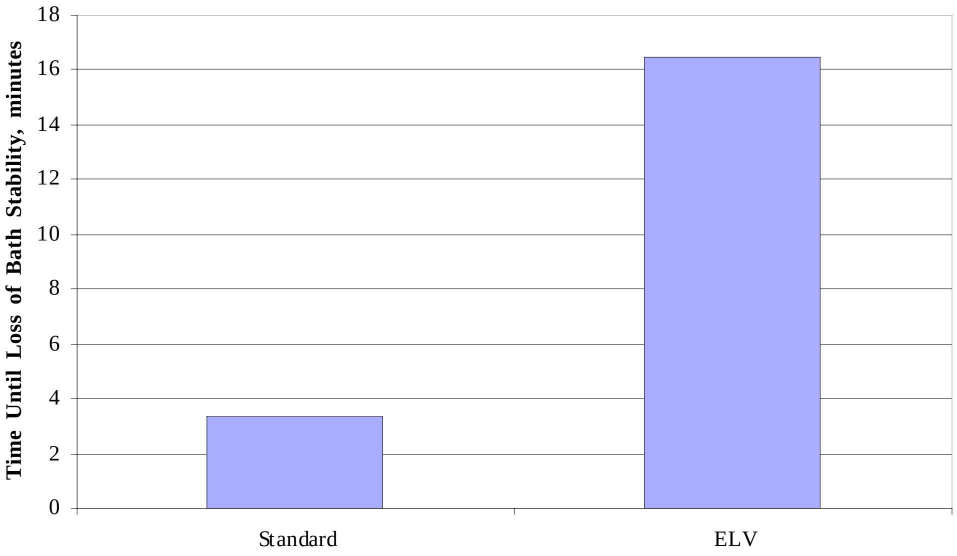

Figure 6: Comparison of Bath Stability between current and ELV-compliant Ni-P-PTFE processes by Palladium Stability Test

For each test, the same concentration of PTFE dispersion was used and held at a constant temperature of 80^{o}C. The palladium stability test involves adding at the start and after each minute of the test, 0.2mL of a solution consisting of 125 mg/L $PdCl_2$ and 20 mL/L HCl. The test is stopped when the bath begins to decompose and the time is recorded. By this method of evaluating the stability of an electroless nickel bath, the ELV process is five times more stable than the current process.

Black Electroless Nickel

Black Electroless nickel was first introduced in the early 1980's by immersing the electroless nickel-plated material into a nitric acid solution.[4] This produced a very black coating with minimal wear characteristics. Figure 7 shows the surface structure of a typical black electroless nickel coating processed with nitric acid as the blackening agent.

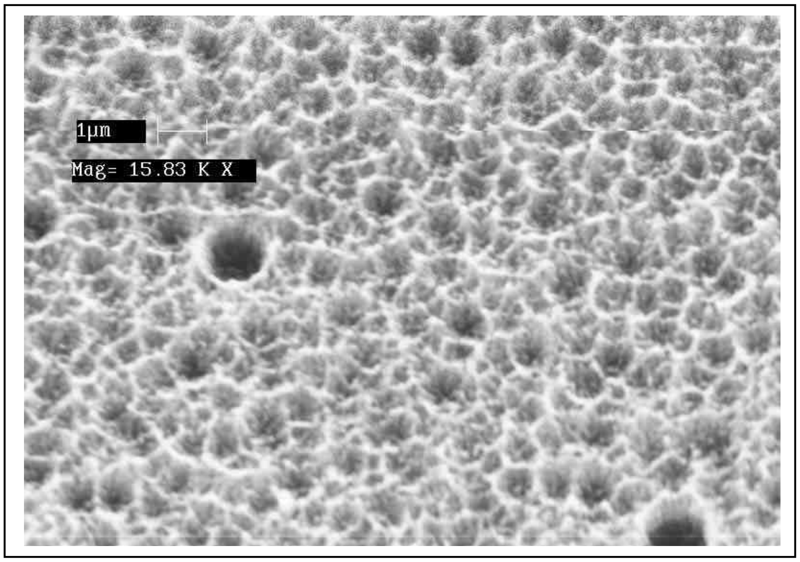

Figure 7. Typical structure of black EN processed in nitric acid, 15,000X

Using nitric acid as the blacking agent produces a structure with a stalagmite-like morphology. In addition these deposits tend to be very powdery and fragile. The stalagmite-like coatings are therefore easily broken off from the base electroless nickel coating.

Looking at the standard for black electrodeposited coating, black chromium, and the structure is very feathery and powdery also. The surface morphology of the black chromium coating is shown in Figure 8. This surface is very different from the black electroless nickel surface. Whereas the black electroless nickel surface has very pronounced crater surface the black chromium has more of a dendritic morphology. In addition both the black chromium and black electroless nickel from the nitric acid dip posses very fragile crystal structure that are easily worn away with handling.

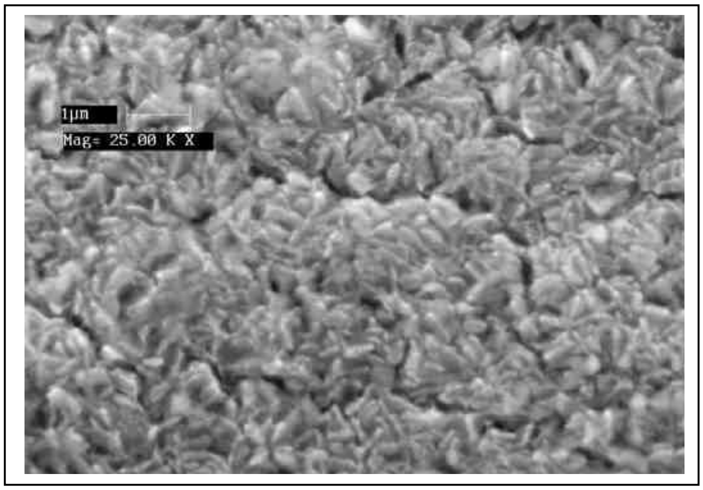

Figure 8. Black chromium surface 25,000X.

The surface morphology of the new black electroless nickel process is completely different than that of the nitric acid processed electroless nickel and the black chromium. Figure 9 shows the surface structure of the new black electroless nickel coating. The nitric acid based blacking solution and the black chromium show very textured surface the new black electroless nickel surface is very smooth.

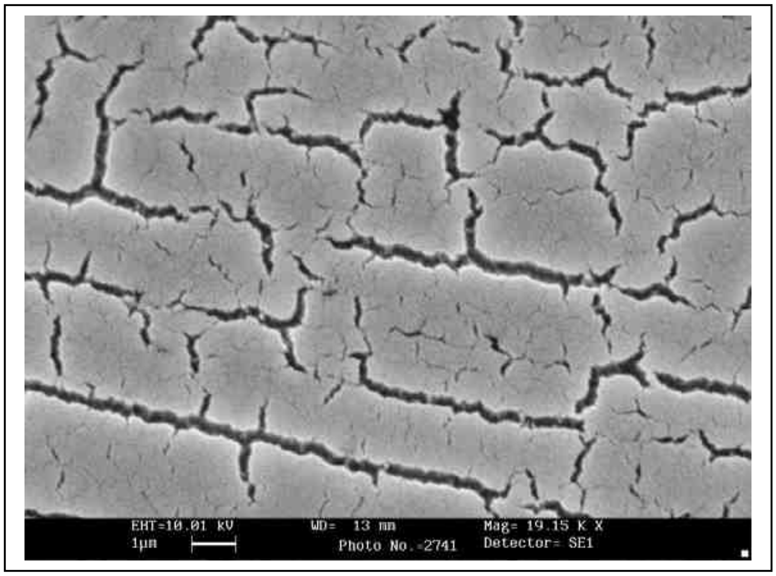

Figure 9. Surface of new non nitric black electroless nickel.20,000X

Measuring the color of this black coatings, is slightly different than how previous work has shown the blackness of the coatings.[5] The color of the deposits were measured on a color spectrophotometer using the CIELAB convention. The CIELAB formula and its associated color space are based on a coordinate system that contains three (3) coordinates: L*,A* and B*. The L* represents lightness (white to black), the A* represents redness-greeness and the B* represents yellowness-blueness. These coordinates were chosen because they represent how the receptors in our eyes code the perceived color to our brain. We will not perceive a color as being both red and green (or yellow and blue). We may see colors as yellow and red at the same time (orange), but not green and red. Therefore, numbers can be assigned to these coordinates to represent the perceived color.

Measuring the black chromium deposit on the color spectrophotometer one can see various color forming as the plating time is increased. The sample with the least amount of time shows more red color in the coating then the samples with longer plating time. Figure 10 shows these results of the black chromium deposit.

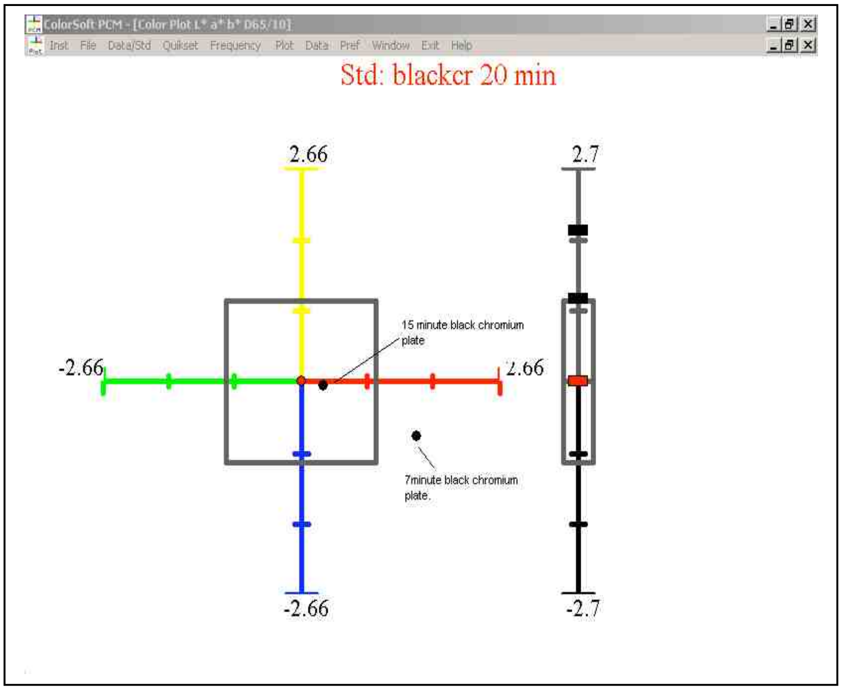

Figure 10. Color spectrum of black hexavalent chromium deposit.

Inserting the black electroless nickel value into the black chromium chart there is a significant change. The black chromium deposit is significantly lighter than the black electroless nickel coating. Figure 11 shows this shift.

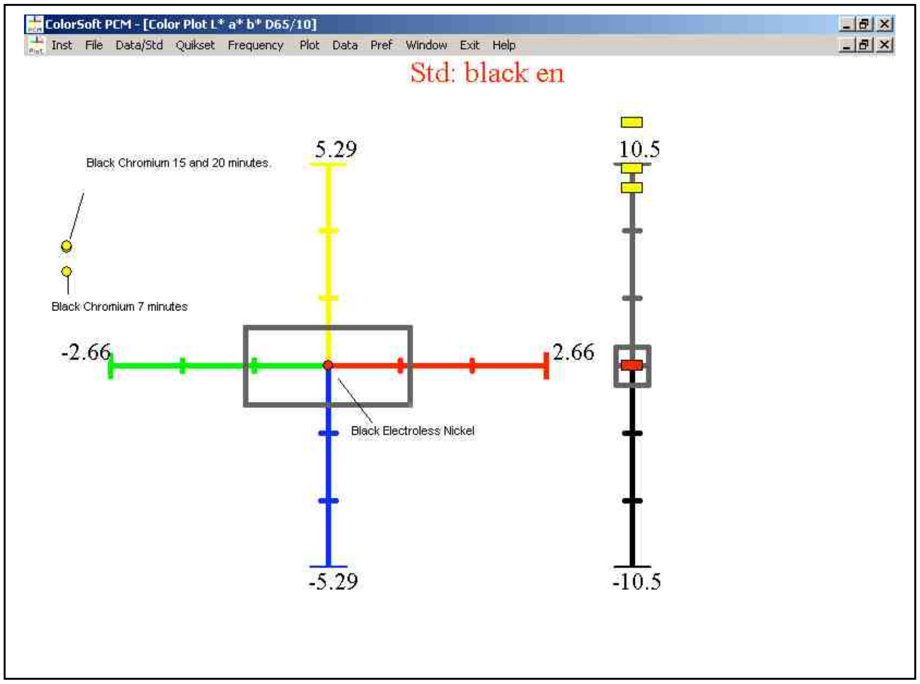

Figure 11. Color chart of black EN and Black Chromium

Looking at this data in table form, Table 2,shows that the Black EN is significantly darker, L* than the Black chromium coatings, in addition, the Black chromium coatings are greener and yellower than the Black EN deposit.

Coating	X	Y	Z	L*	a*	b*	DE*
Black EN	0	0	0	0	0	0	0
Black Cr 20 minutes	1.06	1.32	1.34	9.25	-5.89	3.1	11.4
Black Cr 15 minutes	1.25	1.52	1.58	10.28	-5.6	3.1	12.1
Black Cr 7 minutes	1.47	1.7	1.89	11.1	-4.35	2.46	12.2

Table 2.Data comparison between Black EN and Black Cr.

The definition of the various terms are as follows, the L* indicates lightness and darkness. A negative value would indicate a darker color and a positive value would indicate and lighter color. From this data the black chromium values are all positive to the black electroless nickel deposit and therefore are lighter in color. The a* indicates green-red and all the black chromium coating is greener than the black EN. The b* indicates yellow-blue color and the black chromium coatings are yellower the black EN deposit. The final term DE* indicates total color difference and this shows that the black chromium deposit has a significant color difference to the black EN deposit. Typically a value of two (2) for DE indicates no perceivable difference in color. The values for the black chromium are all greater than 10 which indicates a significant color difference.

Next the wear resistance of the black EN was compared to other various black deposit, black chromium, black zinc chromate, black nickel, and black iron. The panel were plated on mild steel plates. Wear test was performed by the Suga Wear Test method with a 400 g load and 400 times rubbing the part left to right.
Table 3 list the results.

Treatment	Percentage Exposure of Base Material
Black EN	25%
Black Zinc	40%
Black Chromium	25%
Black Nickel	100%
Black Iron	30%

Table 3. Wear data of various coatings.

The corrosion resistance of the black EN was also compared to the other various black coating by neutral salt spray testing by ASTM B-117, and performed well. Table 4 shows the results.

Coating	Test Time (Hrs)					Results
	2	4	50	100	150	
Black EN	10	10	10	10	10	No rust
Black Zn	10	10	10	10	9.5	White
Black Cr	10	10	10	9.8	-	Red rust
Black Ni	10	9.5	-	-	-	Red rust
Black Fe	9.5	-	-	-	-	Red rust

Table 4. Corrosion results of various black coatings

Conclusion

Development of ELV-compliant technology has allowed for improvements upon current technology to be not only more environmentally friendly, but also offer performance improvements. This paper described two new ELV compliant electroless nickel process and showed the benefits of these processes.

Electroless nickel deposition offers many advantages over electrolytic processing. Combining these benefits with the superior corrosion resistance and lubricity that PTFE offers in the form of a composite coating results in a process that is unique and cannot be matched by other plating processes. In addition the new black electroless nickel process showed unique properties as compared to the standard black plating processes that are currently used.

References

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