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Investigation of the Blackening Process of Electroless Nickel-Phosphorous Coatings and Their Properties

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ABSTRACT

Electroless black nickel-phosphorus plating is an advanced electroless nickel plating process formulated to deposit a black finish when processed through an oxidizing acid solution. Optimum immersion time, temperature of the oxidizing acid solution, post-heat treatment and the top coating are discussed. Morphology and components of pre-etch and post-etch were compared to examine the phosphorus, nickel, oxygen and sulfur contents on the preparation of black surfaces by dispersive x-ray microanalysis and scanning electron microscopy. The corrosion resistance of the black electroless nickel-phosphorus was investigated by polarization measurements and salt spray testing.

Keywords: Electroless nickel-phosphorus, black nickel-phosphorus, black finishes

Introduction

Electroless nickel alloys are applied because of their useful physical and mechanical properties.[1,2] Black electroless nickel coatings which are used in optical instruments, absorbing material, decorative coatings and aerospace industries are specified due to their stability against sunlight exposure, electrical conductivity and wear resistance.[3]

The black coating is formed by oxidization of a low nickel-phosphorus alloy. This alloy is proposed for its improved wear resistance and deeper black finish when compared to medium or high phosphorus alloys.

Experimental

Steel Hull cell panels processed with a proprietary electroless nickel** was used to study the blackening coating and its properties. First the panels were plated in high nickel-phosphorus for one hour to increase the corrosion resistance. They were then plated in low phosphorus-nickel for a one additional hour. Following water rinsing, they were immersed in the oxidizing solution. The immersion time was studied, including 30 sec, 1 min, 2 min and 5 min. The temperature of the solution was varied at 25°C, 35°C and 50°C. The parts were subsequently rinsed and dried. Heat treatment was performed at 190°C for 2 hr.

Investigative techniques included dispersive x-ray microanalysis (EDX) and scanning electron microscopy (SEM), which was also used to measure cross-section thicknesses. The results were analyzed to determine the optimum immersion time, temperature, post-heat treatment and top coating. The deposit morphology and the components of the pre-etch and post-etch processes were compared to examine phosphorus, nickel, oxygen and sulfur contents on the black surface. The corrosion resistance, with and without heat treatment, with and without top coatings, was also investigated by salt spray test in 5% NaCl solution for 48 hr. The black coating abrasion resistance was check by a finger rub test, ten times on each sample. Finally, the electrochemical corrosion resistance, with or without heat treatment, was made using a potentiostat.***

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**NiKlad Eclipse®, MacDermid, Inc., Waterbury, CT 06702.

***The 300 mL conventional three-electrode cell comprised the pre-etching and post-etching Ni-P coating as the working electrode, a silver/silver chloride (3M KCl) as the reference electrode and platinum as the counter electrode. All sample surfaces were slightly wet ground with 600 grade emery papers, washed with distilled water, degreased with acetone and dried in air. Prior to scanning, all samples were immersed in the electrolytes and the cell was left for at least 10 min

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Results and discussion

Effect of immersion time on as-processed black Ni-P

The black color of Ni-P coating arises from its unique surface morphology combined with the formation of nickel oxides and nickel phosphate.

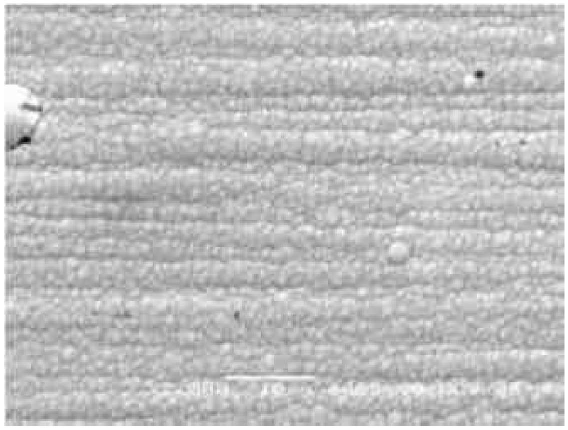

Figure 1 - As-plated low phosphorus Ni-P† coating (2000×).

Figure 1 shows that low phosphorus alloys produce a nodular morphology. After the black etching, these nodules are gradually etched away with increasing etching time, seen in Fig. 2 (etching temperature, 25°C with gentle agitation). Surfaces etched for 2 min and 5 min became smoother, and the nodular structures were enlarged. Some cracks on the black Ni-P surface can be seen after the black treatment.

The phosphorus, sulfur, oxygen and nickel contents of pre-etch and post-etch Ni-P coating with various etching times are shown in Table 1. From this table, we can see that the phosphorus and oxygen contents increased, whereas the nickel content decreased with an increase in immersion time. This suggests that only nickel atoms in the nodular surface were preferentially removed and some nickel atoms formed oxides such as NiO and Ni_2O_3. This caused the phosphorus and oxygen contents to increase at the black Ni-P surface.

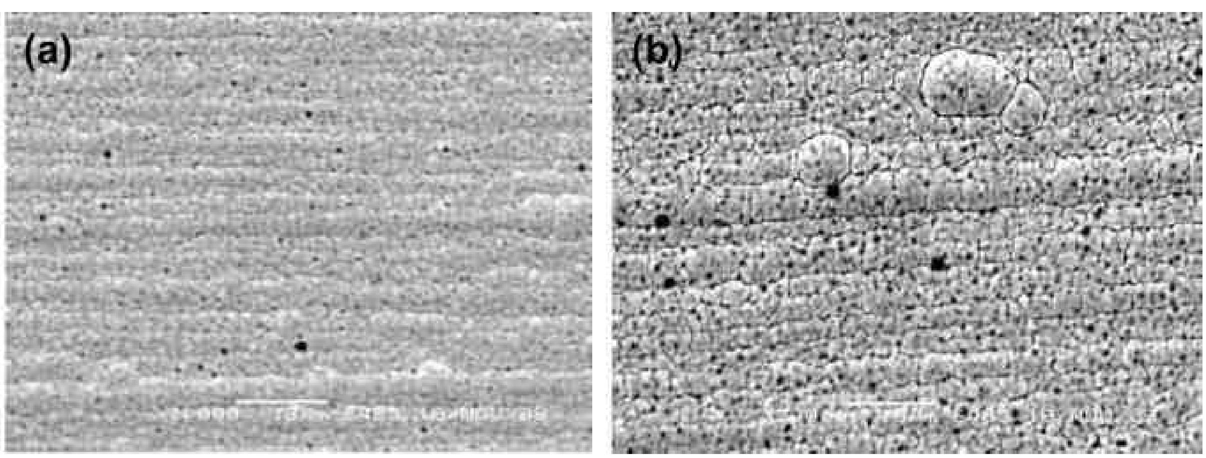

Figure 2(a,b) - Surface morphology of black Ni-P coatings with immersion time: (a) 30 sec, (b) 1.0 min.

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to stabilize the open-circuit potential (OCP). Polarization curves were measured at a scan rate of 1 mV/sec starting from -250 mV to 1 V with respect to the OCP in 5% NaCl.

† NiKlad® ELV 824, MacDermid, Inc., Waterbury, CT 06702.

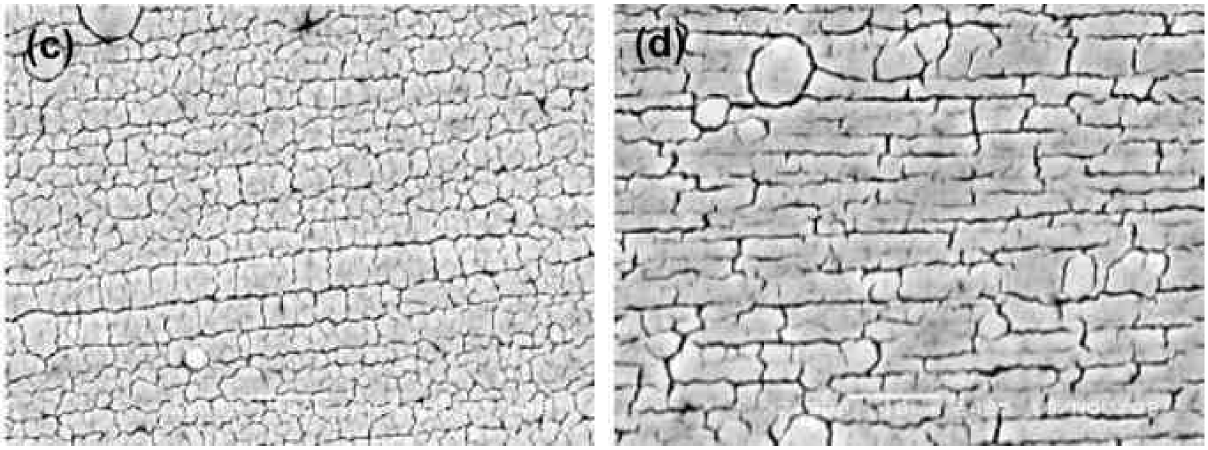

Figure 2(c,d) - Surface morphology of black Ni-P coatings with immersion time: (c) 2.0 min and (d) 5.0 min; temperature, 25°C (2000×).

Table 1 - Composition of as plated low phosphorus Ni-P and black Ni-P coatings with various etching times at 25°C.

Black Ni-P					
Etching time	0	30 sec	1.0 min	2.0 min	5.0 min
Composition (wt%)					
Ni	75.71	73.35	70.94	64.71	59.54
P	1.33	2.59	3.94	7.28	10.14
S	0.24	0.29	0.28	0.39	0.40
O	22.72	23.77	24.84	27.62	29.92

The variation in the intensity of the black finish with the immersion time is shown in Fig. 3. At 30 sec, coating iridescence is noted [Fig. 3(a)]. At 1.0 min, there is a slight iridescence noted on the black Ni-P coating [Fig. 3(b)]. The iridescence phenomenon is caused by the nodules not being completely etched away [Figs. 2(a) and (b)]. At longer immersion times of 2.0 and 5.0 min [Figs. 3(c) and (d)], the black Ni-P coatings were iridescence-free, and intense black. They benefit from a smoother surface and larger nodular structures.

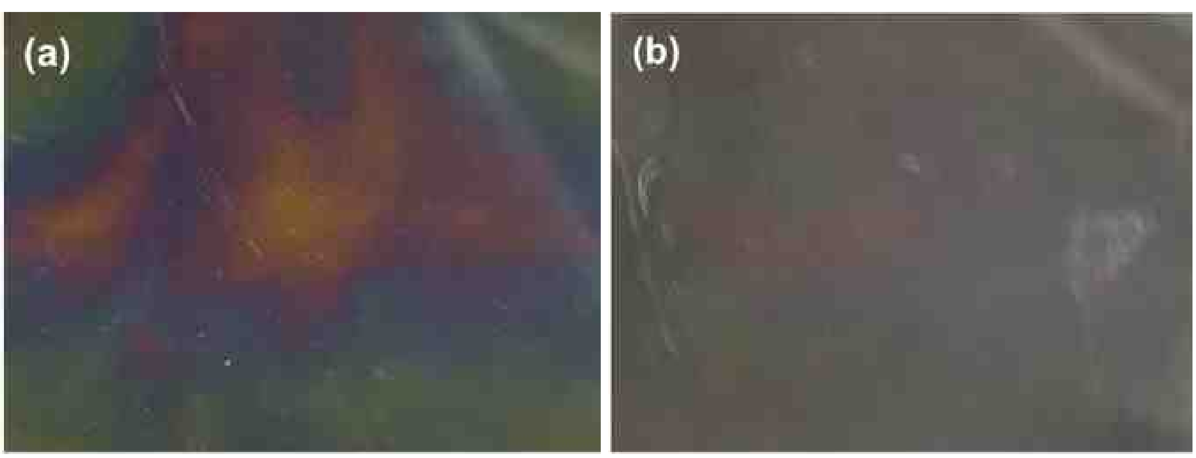

Figure 3(a,b) - Iridescence of black Ni-P coatings with immersion time at 25°C: (a) 30 sec, (b) 1.0 min.

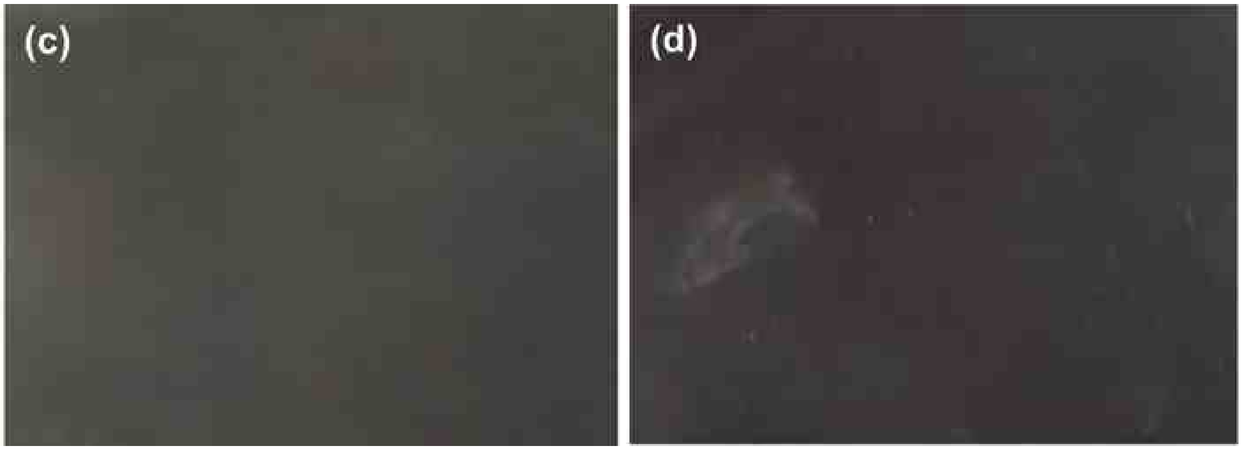

Figure 3(c,d) - Iridescence of black Ni-P coatings with immersion time at 25°C: (c) 2.0 min and (d) 5.0 min.

It is not easy to measure (black film) hardness because the thickness of this black layer is less than 1 µm (Fig. 4). Therefore, the finger rubbing method (ten double rubs per each sample) was employed to check abrasion resistance. The results show that improved abrasion resistance was achieved with increasing immersion time. However, some defects were seen at the edge of coating at an immersion time of 5 min. Therefore the optimum immersion time was taken to be 2 min.

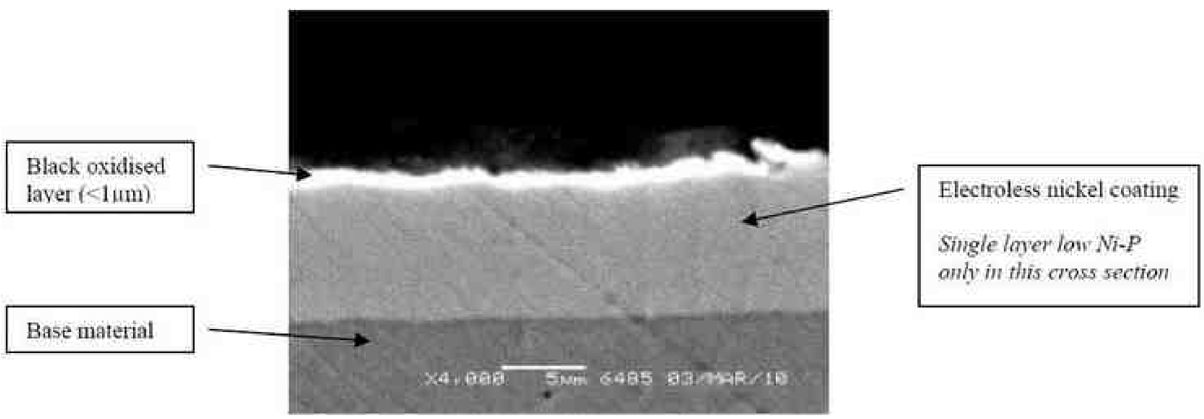

Figure 4 - Cross section of nickel-phosphorus coating and the oxidized black layer.

Effect of temperature of etching solution on as-processed black Ni-P

Figure 5 shows the effect of temperature (25°C, 35°C and 50°C) on the black coating. The nodular structure becomes slightly larger with increasing temperature of the etching solution.

Table 2 - Composition of black Ni-P with various etching temperature, post-heat treatment and salt spray test in 5% NaCl.

Black Ni-P					
Sample condition	35°C etching	50°C etching	HT 190°C/2 hr	5% NaCl Salt Spray	HT + Salt Spray
Composition (wt%)					
Ni	63.63	62.62	65.80	68.92	67.71
P	7.84	8.39	6.72	5.05	5.66
S	0.42	0.44	0.35	0.29	0.35
O	28.11	28.55	27.13	25.74	26.28

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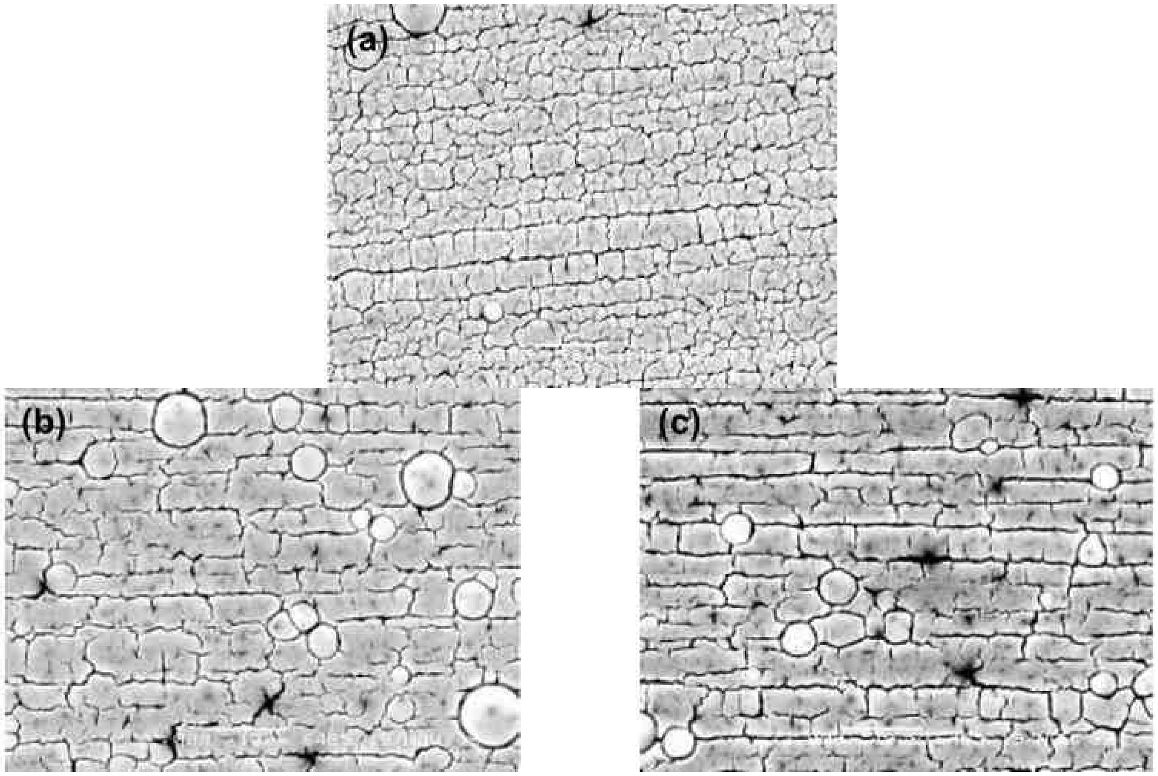

Figure 5 - Surface morphology of black Ni-P coatings with a 2.0-min immersion time: (a) 25°C, (b) 35°C and (c) 50°C.

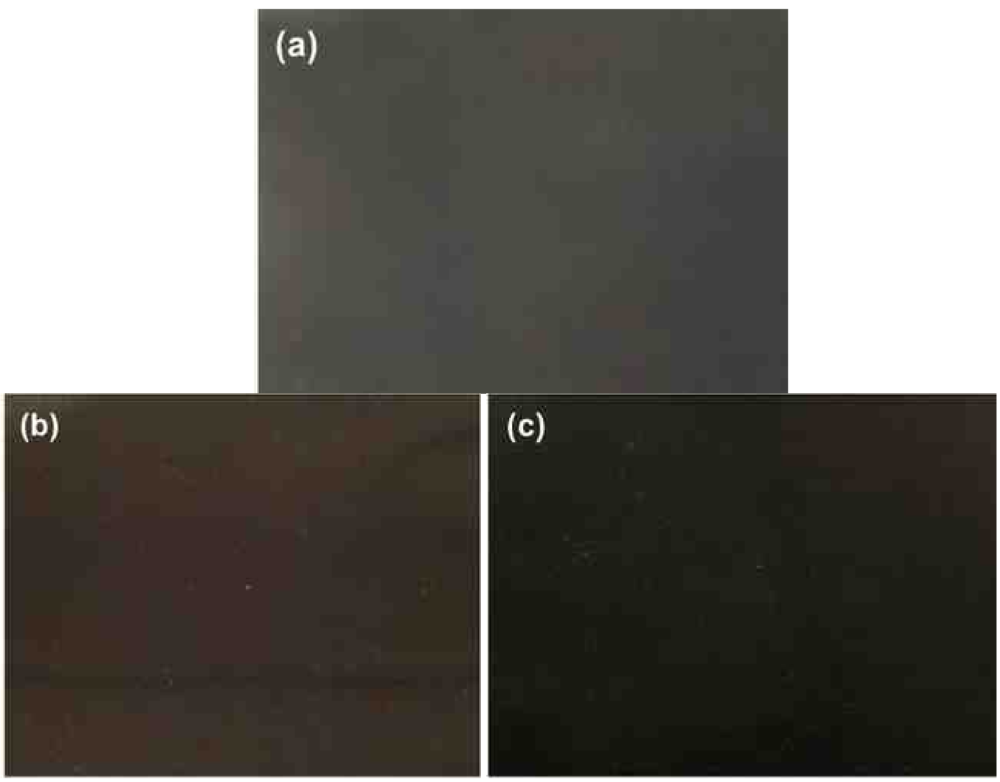

Figure 6 - Surface appearance of black Ni-P coatings with a 2.0-min immersion: (a) 25°C, (b) 35°C and (c) 50°C.

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Effect of heat treatment on as-processed black Ni-P

Figure 7 shows the morphology of a black Ni-P coating with a 2.0-min immersion time at 25°C, and a heat treatment at 190°C for 2.0 hr. Compared with the corresponding non-heat treated sample shown in Fig. 5(a), the nodular structures are slightly larger with deeper cracks. Although the elemental contents pre- and post-heat treatment were similar (Tables 1 and 2), the post-heat treated samples show increased abrasion resistance. Therefore heat treatment is proposed to take advantage of this, with an additional benefit of stabilizing the black color.

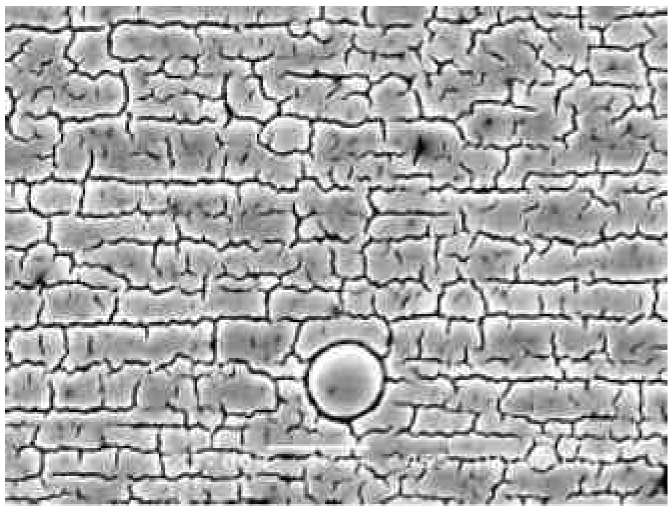

Figure 7 - Surface morphology of a black Ni-P coating with a 2.0-min immersion time at 25°C and heat treated at 190°C for 2.0 hr (2000×)

Salt spray testing of as-processed black Ni-P

Following 5% neutral salt spray test for 48 hr, to maintain the intensity of the black color, a top coat is recommended. This can be seen in Fig. 8, which compares an untreated Ni-P coating, a black coating (no topcoat before and after heat treatment) and a black coating with an organic topcoat.

Electrochemical corrosion resistance of as-processed black Ni-P

Figure 9 compares the polarization curves of the "standard" and black oxidized (with and without heat treatment) coatings in 5% NaCl.

The findings from this test show that all three coatings exhibit passivation behavior, although they differ from one another in the nature of transition from active to passive state. The untreated low Ni-P coating undergoes a wide active-passive transition and becomes passive just above the open circuit potential and remains passive through about 0.7 V difference. Black Ni-P coatings with and without heat treatment have a narrow active-passive transition. The passive difference of both black Ni-P coatings is 0.7 V and 0.5 V, respectively. Further, the black Ni-P coatings with and without heat treatment, show a higher corrosion current because the black layer is very thin and has the special crack structure, as seen in Table 3. The black Ni-P coating without heat treatment shows slightly higher corrosion potential and passive potential compared to that of the black Ni-P coating with heat treatment (Table 3). This indicates that heat treatment can improve the corrosion resistance of black Ni-P coatings, by reducing the current density of the black Ni-P layer. It also can explain that black Ni-P with heat treatment in Fig. 8(c) only lost partial color, compared to the black Ni-P without heat treatment in Fig. 8(b). It should be noted that all three coatings provide additional corrosion resistance at a higher potential due to the presence of a high-phosphorus Ni-P anti-corrosion coating underneath.

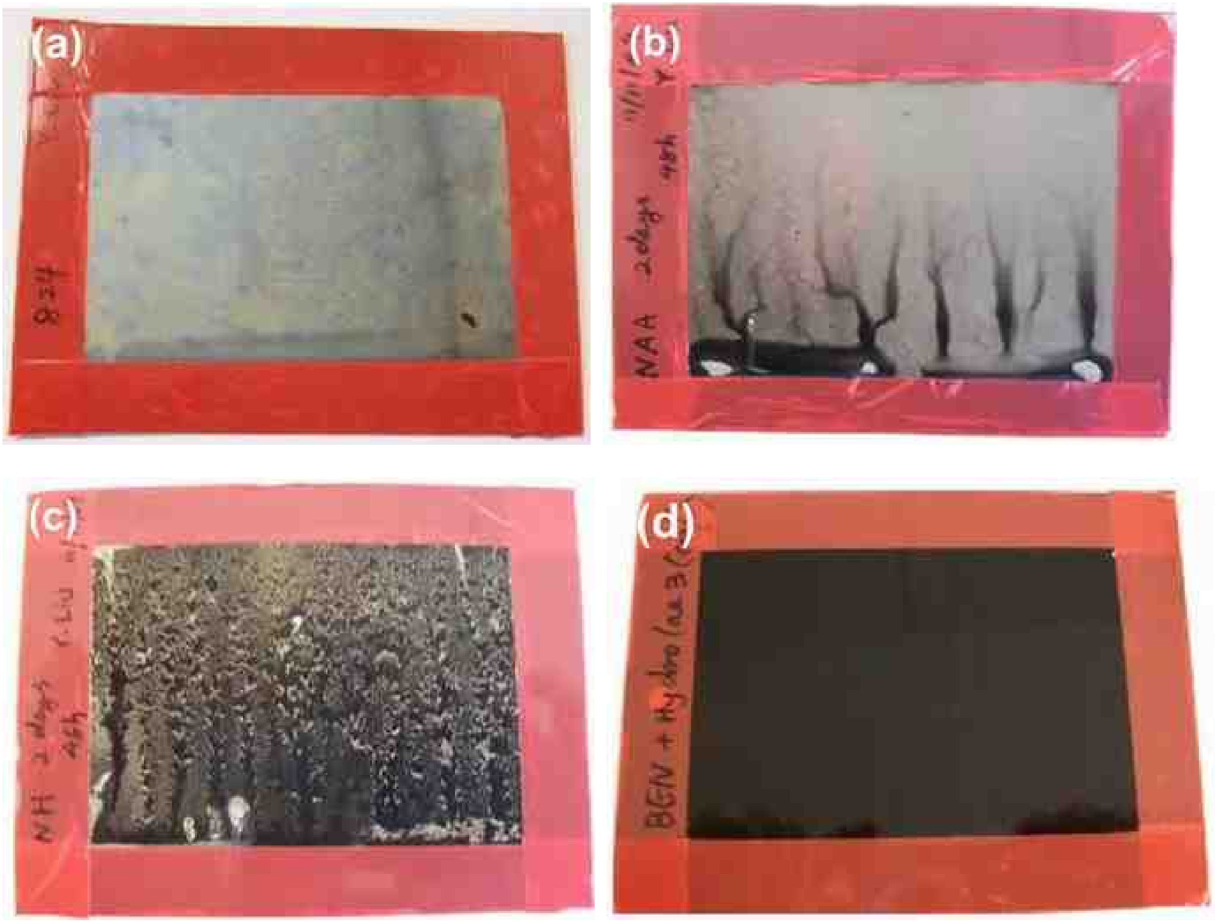

Figure 8 - Results of 48-hr 5% NaCl salt spray testing: (a) Ni-P coating with no oxidization treatment, (b) black oxidization without heat treatment, (c) black oxidization with heat treatment and (d) with organic topcoat.

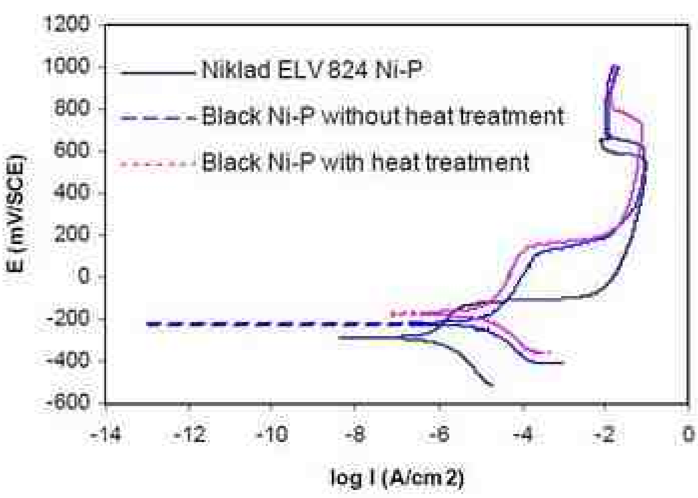

Figure 9 - Polarization curves (in 5% NaCl) of a low-phosphorus Ni-P coating, and black Ni-P coatings with and without heat treatment.

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Table 3 - Corrosion potential and corrosion current values (in 5% NaCl) obtained from the polarization curve in Fig. 9 of a low-phosphorus Ni-P coating, and black Ni-P coatings with and without heat treatment.

Coatings	E_{corr} (mV)	I_{corr} (μA/cm^2)	β_a (V/decade)	β_c (V/decade)
Low-phosphorus Ni-P	-284.9	2.303	856.8E^{-3}	255.9E^{-3}
Black Ni-P without heat treatment	-216.8	20.98	300.4E^{-3}	203.4E^{-3}
Black Ni-P with heat treatment	-173.6	10.36	278.4E^{-3}	137.6E^{-3}

Conclusions

Black Ni-P coatings were prepared in an oxidizing (etching) solution after the electroless plating process. During etching, nodules of the electroless Ni-P coating containing 1.0-3.0 wt% P are etched away. The surfaces become smoother and the nodular structures become larger. Phosphorus and oxygen contents increase and the nickel content decreases. This suggests that only nickel atoms in the nodule surface are preferentially removed and some nickel atoms form oxides such as NiO and Ni_2O_3.

Black Ni-P coatings show slightly higher corrosion potential and passivation potential when compared to untreated Ni-P coatings. Regardless of whether a heat treatment is applied, they show a higher corrosion current because the black layer is very thin and has the special crack structure. Nonetheless, heat treatment is recommended to harden the black layer and stabilize the deposit color. Heat treatment also can slightly improve the corrosion resistance of the black Ni-P coating.

Considering the optimum abrasion resistance, color, adhesion and economic considerations, the optimum immersion time is 2.0 min and the optimum temperature of the etching solution is 25°C. As black Ni-P coatings lose some of their black color during the salt spray test (48 hr), an organic top coat is proposed. This will help retain deposit color and luster in harsh environments.

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About the authors

Duncan Beckett is the Global Marketing Manager for Engineering Coatings at MacDermid. Duncan has an honors degree in Chemistry, which was gained while working as a chemist at 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 in 2006.

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David Hawthorne is a Senior Electroplating Specialist working in MacDermid's R&D Process Development Centre in Birmingham. He first began working for a company specializing in decorative plating in 1989 before joining Wm. Cannings in 1995, working in their customer demonstration area. David later became Manager of the MacDermid's UK service laboratory before moving to his present role. He has a HNC in Physical Science as well as industry based qualifications awarded by the IMF.