Industrial Implementation of Nanostructured Cobalt-Phosphorus Coatings at Enduro Industries LLC

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ABSTRACT

Electrolytic Hard Chromium plating (EHC) has been facing increasing environmental and health and safety regulations. In response to the need for alternatives, since 2007 Enduro Industries LLC, a leading supplier of EHC-coated hydraulic bars has been supplying nanostructured cobalt-phosphorus (Nanovate™ CO) coated steel bars and tubing for applications currently serviced by EHC in the fluid power market.

Nanostructured Co-P (nCoP) is an environmentally compliant alternative to EHC coatings. As an electrodeposition process, nCoP is fully compatible with the existing EHC infrastructure, but exhibits higher cathodic efficiencies and deposition rates than EHC, thus yielding higher throughput, reduced plant footprint and reduced energy consumption. Further, nCoP offers significant performance enhancements over EHC including superior sliding wear, lubricity, corrosion protection and fatigue resistance.

The nCoP production facility at Enduro Industries LLC will be showcased, with emphasis on process control and production capabilities. Performance data from laboratory testing and case studies from field use will highlight the benefits of nCoP over EHC.

INTRODUCTION

HARD CHROME

Hard chrome, also known as *industrial/engineering chrome or electrolytic hard chromium* (EHC), is employed as a functional coating for the enhancement of surface performance in engineering applications requiring low friction, wear and corrosion resistance. EHC is typically applied from 0.00025-0.010 inches in thickness. Thin deposits are normally used to substantially increase the life of components in wear applications or corrosive environments. Thick deposits are used for salvage and repair of worn, damaged or mis-machined components. Common applications for EHC include hydraulic and pneumatic piston rods and cylinders, actuators, pump shafts and rotors, plastic and rubber rolls, moulds, dies and screws. [[1]]

The EHC plating process is mature, well-understood and cost-effective. However, copious amounts of hexavalent chromium aerosols or fumes are generated during processing. There has been pressure in the electroplating industry from environmental and worker safety agencies to find more environmentally benign alternatives to hard chrome, following a decision by the U.S. Department of Labor’s Occupational Safety and Health Administration (OSHA) to reduce the permissible exposure limit (PEL) for hexavalent chromium, a known carcinogen. To meet

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these regulations, significant capital investment towards appropriate health and safety equipment and waste remediation has been required. [2,3]

In addition to health and safety concerns, EHC exhibits several technical drawbacks. As a result of its low electrolytic efficiency, deposition (or build up) rates are relatively low compared to the plating rates of other metals (e.g., 0.0005”-0.001” per hour for EHC versus > 0.002” per hour for nickel). Furthermore, EHC imparts a significant fatigue life debit and, when applied to high strength steels, can cause hydrogen embrittlement thus necessitating the application of a post-plating relief bakeout. EHC deposits are micro-cracked which results in poor corrosion protection of underlying substrates, particularly when employed without a nickel plated underlayer. [4]

HARD CHROME ALTERNATIVES

EHC alternative technologies include: thermal spray, plasma vapor deposition, and chromium-free coatings applied by electrolytic or electroless plating techniques. [5,6,7] Over the last 10 years, tungsten carbide-cobalt (WC-Co) and similar materials applied using high-velocity oxygen-fuel (HVOF) have generally been accepted as suitable alternatives for EHC in the aerospace industry for low volume, high-added-value line-of-sight (LOS) coating applications. [8] However, HVOF deployments require significant capital expenditures, special application equipment and personnel training. For coating applications requiring non-line-of-sight deposition (NLOS) and/or high-volume, low-value-added production, it is generally agreed that electroplating technologies are suitable and cost-effective.

Nanovate™ CO is a nanostructured cobalt-phosphorus alloy (nCoP) that has been developed by Integran Technologies, Inc. (Integran) as an alternative to EHC for both LOS and NLOS coating applications. [9,10,11]

Integran’s nanostructured metals and alloys are produced by a patented electrodeposition process. These materials have an average grain size of <100 nm (see Figure 1) and benefit from the Hall-Petch strengthening mechanism. [12,13,14,15] They are fully dense and show improved hardness (3-5X increase), yield strength (5-9X increase), ultimate tensile strength (3-5X increase) and coefficient of friction (up to 50% reduction). These properties have tremendous possibilities in enhancing material performance in a variety of applications.

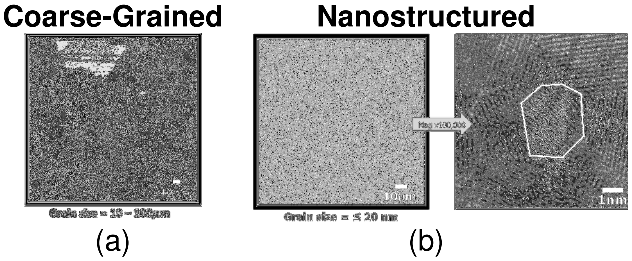

Figure 1: Electron micrographs of (a) a coarse-grained metal [16] and (b) Nanostructured material (left) and magnified x100,000 (right). A single grain of the nanocrystalline metal is outlined.

NANOSTRUCTURED COBALT PHOSPHORUS HARD CHROME ALTERNATIVE

PROCESS COMPARISON

Table 1 demonstrates the significant process improvements offered by nCoP over EHC. As nCoP is produced by electrodeposition, it represents a “drop-in” alternative technology that is fully compatible with the current EHC infrastructure and is well-suited to LOS and NLOS surfaces. However unlike EHC, the nCoP process utilizes environmentally compliant materials and does not generate hazardous emissions or by-products. The high cathodic current efficiency and plating rate of nCoP result in a significant reduction in the energy consumption and an increase in production throughput in comparison with EHC.

Table 1: Comparison of nCoP and EHC Processes.

	nCoP	**EHC**
Deposition Method	Electrodeposition	Electrodeposition
Applicable Geometries	LOS and NLOS	LOS and NLOS
Efficiency	85-95%	15-35%
Deposition Rate	0.002”-0.008” per hour	0.0005”-0.001” per hour
Emission Analysis	Below OSHA limits	Cr^{+6}

MATERIAL PROPERTIES

Table 2 show the properties of nCoP compared to those of EHC. Visually, nCoP coatings are uniform and shiny, similar to EHC. Unlike EHC, however, the nCoP coatings are fully dense and free of pits, pores or cracks. Metallurgically, nCoP exhibits a hexagonal close-packed structure, the equilibrium structure typically found in conventional polycrystalline cobalt at room temperature. The deposit has an average grain size in the range of 5-15nm as observed by direct observation in bright-field imaging using transmission electron microscopy (TEM). As a result, nCoP provides an optimal combination of strength and ductility.

Table 2: Comparison of nCoP and EHC Properties.

	Test Method	**Applicable Standard**	**nCoP**	**EHC**
Appearance	Microscopy	-	Pit/Pore/Crack Free	Micro-cracked
Microstructure	TEM/XRD	-	Nanocrystalline (grain size 5-15nm)	-
Hardness	Vickers Microhardness	ASTM B578	530 – 600 VHN	Min. 600 VHN
			600 – 750 VHN (heat treated)	-
Ductility	Bend Test	ASTM B489	2-7%	<1%
Wear Volume Loss	Pin-on-disc (against Al_2O_3 pin)	ASTM G99	$6 – 7 \times 10^{-6}$ mm^3/Nm	$9 – 11 \times 10^{-6}$ mm^3/Nm
Coefficient of Friction	Pin-on-disc (against Al_2O_3 pin)	ASTM G99	0.4 - 0.5	0.7
Pin Wear	Pin-on-disc (against Al_2O_3 pin)	ASTM G99	Mild	Severe
Corrosion Resistance	Salt Spray	ASTM B117	Protection Rating 8 (1000 h salt spray)	Protection Rating 2 (1000 h salt spray)
Hydrogen Embrittlement	Mechanical Hydrogen Embrittlement	ASTM F519	Pass with bake	Pass with bake
Fatigue	Rotating Beam Fatigue	ISO 1143	Credit vs. EHC, Similar to vs. bare	Significant debit
	Axial Fatigue	ASTM E466	Credit vs. EHC and bare	Significant debit

The nCoP displays significant increases in hardness and strength relative to coarser-grained, conventional cobalt. Through a solid solution hardening mechanism, microhardness values range from 530-600 VHN. A further increase in hardness of up to 750 VHN can be obtained by annealing the as-deposited material. Indeed, as shown in Figure 2, the microhardness of nCoP increases by up to 150 VHN following heat treatment at 375℉, the standard temperature used for hydrogen embrittlement relief baking of high strength steels after plating processes. Interestingly, under these same heat treatment conditions, the microhardness of EHC decreases by 100 VHN. This indicates that although EHC has a higher hardness than nCoP in the as-deposited state, their hardnesses converge at elevated temperatures.

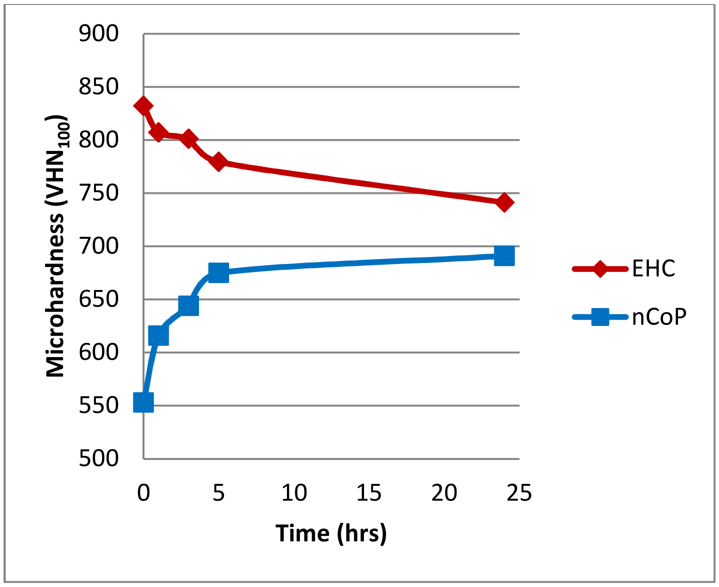

Figure 2: Microhardness of nCoP and EHC after the application of a standard hydrogen embrittlement relief bakeout (375℉) for various times. [11] Reproduced with permission.

As shown in Table 2, nCoP exhibits improved wear loss over EHC in pin-on-disk sliding wear testing. Wear loss of the mating material, in this case an alumina pin, was also less severe. Further, nCoP has a lower coefficient of friction than EHC which is indicative of superior lubricity.

Corrosion resistance in cabinet salt-spray corrosion testing is also improved over EHC. As shown in Figure 3, in a comparison of nCoP and EHC, following 1000hr of exposure in a neutral salt spray (NSS) environment per ASTM B117, the ASTM B537 protection rating decreased to only 8, compared with a rating of less than 2 for EHC. The protection rating is evaluated qualitatively by assessing the quantity of red rust formed on samples. It is worth noting that the nCoP deposit was 50% thinner than the EHC coating used in the test.

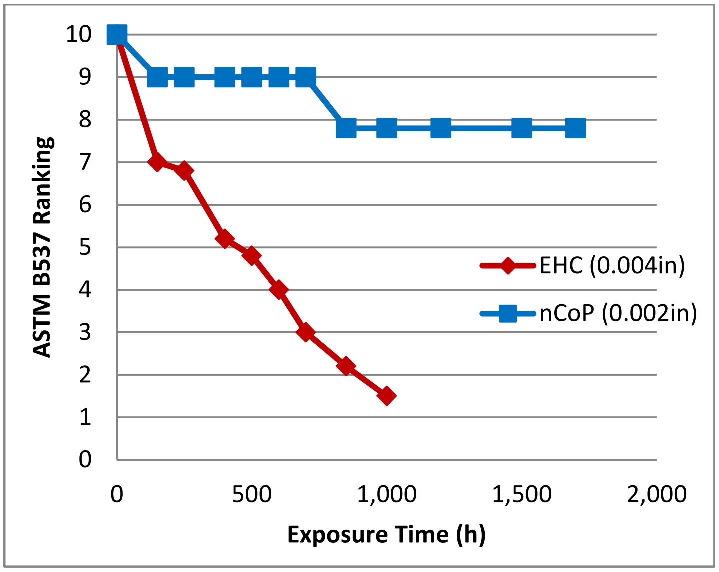

Figure 3: Corrosion protection ranking in salt spray corrosion (ASTM B117). [11] Reproduced with permission.

For high strength steel components, potential for hydrogen embrittlement caused by the electroplating process is an important consideration. The nCoP plating process exhibits a high cathodic current efficiency which leads to significantly less hydrogen generation at the cathode compared with the EHC plating process, thus minimizing likelihood of hydrogen absorption and subsequent hydrogen embrittlement. Mechanical embrittlement tests conducted in accordance with ASTM F519 indicate the standard hydrogen embrittlement relief baking procedures (375°F±25°F for 24hrs) used for EHC can be applied to nCoP to fully eliminate any risk of embrittlement on high strength steel components.

Adhesion of nCoP deposits has been evaluated on a number of substrate materials following suitable activation (e.g., mild steel, high strength steel, stainless steel, nickel-based superalloys, aluminum alloys, etc.). In adhesion tests conducted in accordance with ASTM B 571, deposits showed no signs of peeling or delamination.

INDUSTRIAL IMPLEMENTATION CASE STUDY: ENDURO INDUSTRIES LLC

Enduro Industries LLC (Hannibal, MO) is a subsidiary of PTC Alliance Holdings Corp. and produces and markets EHC-plated steel bars and tubing. In 2007, Enduro Industries LLC (Enduro) and Integran entered into a licensing agreement granting exclusive rights to provide nCoP to the fluid power market. Recognizing the performance advantage offered by nCoP, Enduro opted to become an early adopter of the technology and to continue its leadership in the marketplace in offering innovative and environmental responsible products. nCoP offers customers high corrosion protection using an environmentally compliant process for those who demand it.

In 2007, an nCoP process line was installed at Enduro and technology transition was facilitated by training and support provided by Integran. A small scale production process line (700 gal in volume) was used to demonstrate the robustness of the process in manufacturing nCoP-coated bar and tube products. It was also intended to allow processing of test samples for use in customer evaluations. Figure 4 shows the current production process line located in Enduro's production facility.

Figure 4: The nCoP production line at Enduro Industries LLC.

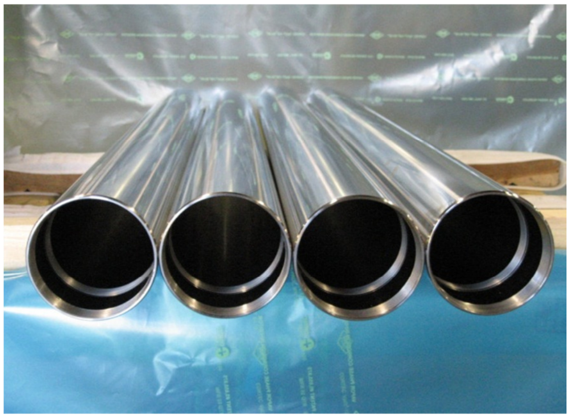

Figure 5: nCoP-coated tubing produced by Enduro Industries LLC.

Enduro currently uses the nCoP production line to produce bar and tubing products between 1-5” in diameter and up to 7’ in length. Figure 5 shows an example of nCoP-coated tubing. Surface hardened, through-thickness hardened and annealed steel materials are offered. Standard finishes with a maximum 12µin Ra are applied to bars and tubing.

The nCoP process stability and robustness have been validated by assessing changes in the coating and solution properties with usage.

For example, Figure 6 shows the nCoP deposit composition, a measure of coating quality and process stability, following system operation for over a year. The coating composition has been found to remain within the operating windows, indicating that the process is stable and operates according to the process specifications.

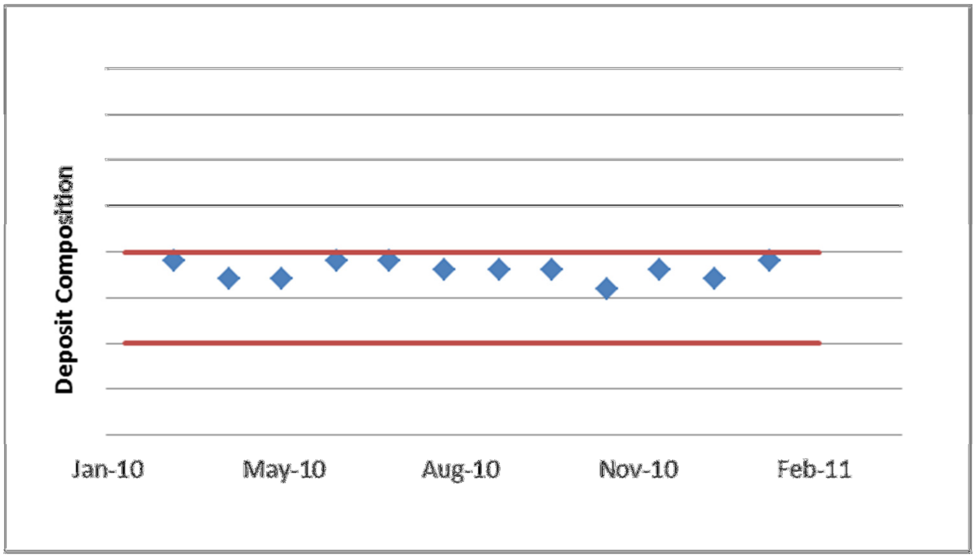

Figure 6: Monthly nCoP deposit composition results. Red lines indicate windows/limits for regular operation.

CUSTOMER PERFORMANCE TESTING

In order to further evaluate nCoP in a production setting, Enduro and its customers have conducted performance testing. This testing has focused on the corrosion, wear, and grindability performance of nCoP.

Corrosion Performance

Tests were conducted in the following environments: neutral salt spray (NSS) in accordance with ASTM B117, copper accelerated acetic acid salt spray (CASS) test in accordance with

ASTM B368, immersion test in concrete remover solution and a custom magnesium chloride spray test.

NSS testing was conducted on nCoP, Enduro's ChromeRod and EHC from various industrial vendors. As shown in Figure 7, nCoP showed no signs of red rust after over 1200 hr exposure, whereas EHC exhibited red rust within as little as 48 hr exposure. Indeed, the ASTM B537 protection rating of nCoP was 10 out of 10 (i.e., no signs of red rust) for test durations greater than 1000hr.

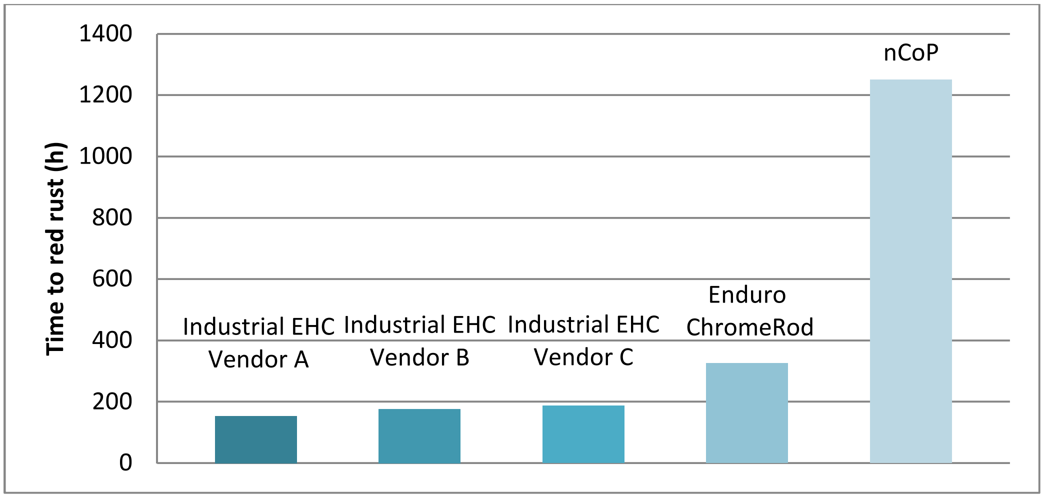

Figure 7: Time to red rust following NSS exposure (as per ASTM B117) for nCoP compared to Enduro Industries LLC's ChromeRod and EHC from other industrial vendor.

CASS testing was conducted on nCoP, Enduro's ChromeRod, multilayer nickel-chrome and EHC from an industrial vendor. As shown in Figure 8, nCoP received a higher protection rating than all other coatings tested, indicative of its superior corrosion performance. Further, CASS testing conducted on nCoP with 0.0015" and 0.002" per side of plate has produced ratings of 9 and 10, respectively, after as much as 64 hrs of exposure. In comparison, a standard EHC product typically failed (rating of 4 to 6 out of 10) after only 24 hrs of exposure in the same environment.

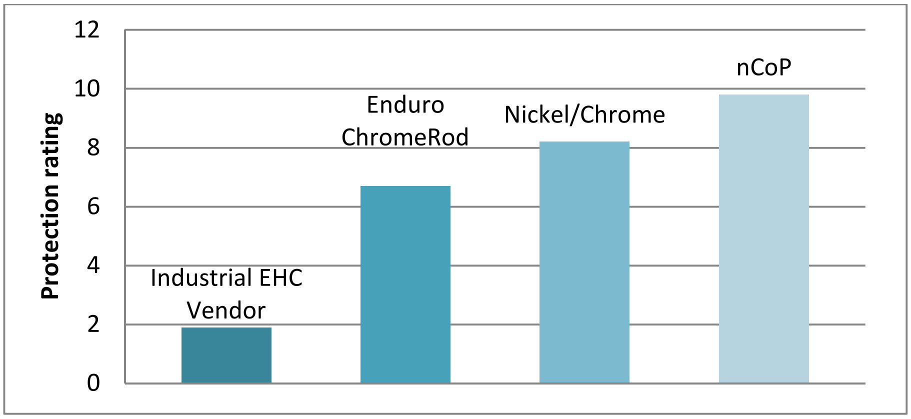

Figure 8: ASTM B537 protection rating after 24hr CASS testing (as per ASTM B368) for nCoP compared to Enduro Industries LLC's ChromeRod, industrial EHC vendor and multilayer Nickel/Chrome coatings.

Immersion testing was conducted on nCoP and EHC to simulate an applicable service environment using a concrete remover solution which can contain high concentrations of hydrochloric acid. ZEP® High Foam Concrete Remover was mixed in a 6:1 ratio with deionized water. The sample diameter was determined before and following immersion for timed intervals of 2hr, 4hr and 20hr, respectively, to determine a rate of removal. Results indicated that the corrosion rate of nCoP was 2x less than that of EHC. Following testing, samples were exposed in the test environment for an additional 2 weeks. The nCoP showed no signs of corrosion following testing.

To assess resistance to magnesium chloride, a compound typically used in de-icing solutions, a custom magnesium chloride spray test was conducted on steel bars coated with nCoP, Enduro's ChromeRod and ChromeRod Extreme, EHC from another industrial vendor, and a high cost nickel-chrome coating.

Testing was conducted over a 30 day period. The test parts were sprayed once per day with the magnesium chloride solution (FreezeGard Zero®) and evaluated qualitatively for evidence of corrosion. After 30 days exposure, the nCoP-coated parts developed a light, clear crystal residue, however, showed no signs of corrosion. By contrast, after only 15 days exposure, the EHC-coated parts (prepared by the industrial vendor) developed green corrosion products indicative of coating corrosion. Figures 9 and 10 shows the appearance of samples following magnesium chloride spray testing for EHC and nCoP, respectively.

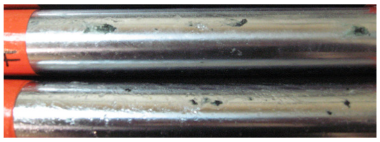

Figure 9: Green corrosion products on EHC-coated steel bars following 15 day exposure to magnesium chloride salt spray testing.

Figure 10: No corrosion products on nCoP-coated steel bars following exposure to 30 days magnesium chloride salt spray testing.

Following completion of testing in the magnesium chloride spray, samples were exposed to theNSS test environment. Figure 11 shows the time to failure for samples. In contrast, the EHC from the other industrial vendor and nitrocarburized samples started to show corrosion after 218 hr and 350 hr respectively, while nickel-chrome samples failed after 500 to 600 hr of NSS testing.

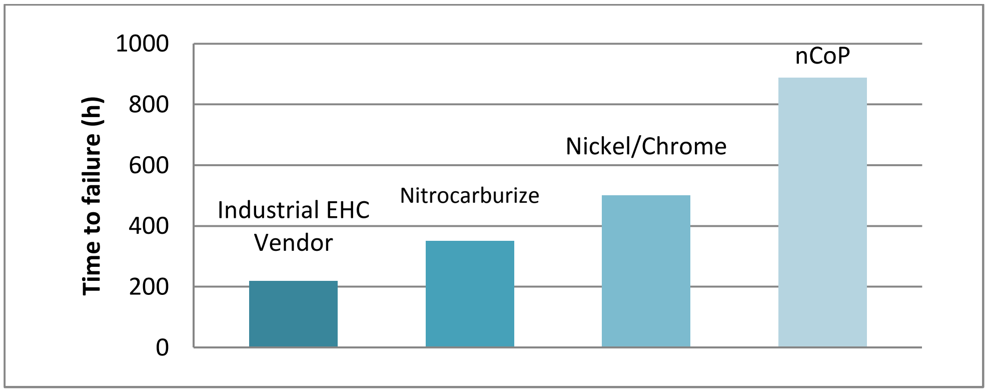

Figure 11: Time to failure in NSS following magnesium chloride testing for nCoP compared to, industrial EHC vendor, nitrocarburized and multilayer Nickel/Chrome coatings.

Wear Performance

The longevity of hydraulic bars in fluid power applications is often determined by the ability to resist hydraulic fluid leakage due to wear between mated rod and seal materials. Testing was completed to evaluate the nCoP coating and its effect on seal leakage compared to Enduro's ChromeRod EHC coating. A pod leakage test protocol was employed in order to evaluate bar-seal configurations. The two-pod test apparatus utilizes a motor-driven crank to simultaneously drive two bars through two identical test pods or pressure chambers (Pod A and Pod B). The pods contain bearings at each end, test seal glands at one end and balance seals at the other end. One test seal sample is installed into each pod. The pods are pressurized as the rod is driven to retract in relation to the test seal sample and depressurized as the rod extends.

Leakage rates were determined by collecting residual fluids and measuring by gravimetric methods. Two seal types were evaluated for testing: polyurethane (b-poly) and rubber-based (z-seal) supplied by SKF Polyseal, Inc. Each coating was tested in both pods up to 200,000 cycles.

Figure 12 shows the average total leakage following 200,000 cycles. No major differences were observed in the leakage rates between nCoP and EHC. This test demonstrated nCoP offers comparable performance to EHC in wear for fluid power applications.

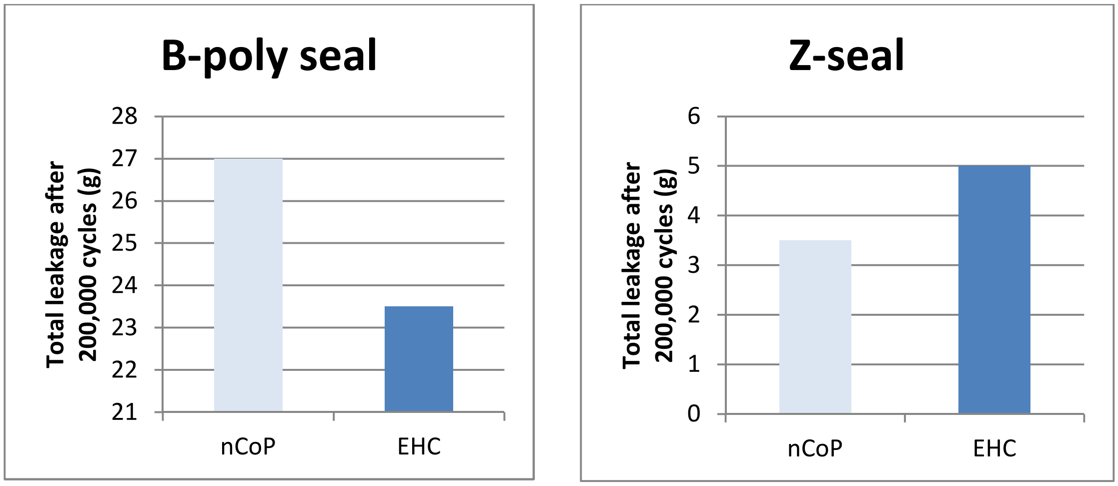

Figure 12: Measured leakage for nCoP and EHC in a pod test. B-poly (left) and Z-seal (right) represent two seal types: polyurethane and rubber-based materials respectively.

Grindability

The grindability of Nanovate™ CR has been evaluated. Using Enduro's standard grinding and polishing processes employed for EHC, it was determined that no additional equipment or processing time is necessary to meet thickness and roughness tolerances currently used for EHC. Enduro is therefore able to offer standard finishes on all nCoP-plated products (12µin Ra maximum).

APPLICATION EXAMPLE

Enduro launched one of its first commercial products with nCoP for a customer manufacturing and supplying fluid power products into the agricultural industry of Western Canada.

Figure 13 shows an example of harvesting equipment where nCoP-coated rods are now employed in place of multilayered nickel/chrome-coated rods. The customer had implemented a program to dramatically improve the corrosion resistance on all their product lines. The customer was experiencing premature corrosion leading to a reduction in service life on their hydraulic cylinder rods used in harvesting equipment. Specifically, they found that one of two nickel/chrome plated rods was always extended or exposed when the unit was rest, leading to corrosion. In addition to corrosion resistance improvement, the application also required the coating for wear resistance. Since the introduction of nCoP into service to replace the nickel/chrome coating in 2008, Enduro's customer has been pleased with the performance of the nCoP plated product. Figure 14 shows nCoP plated rods before subsequent machining and assembly.

Figure 13: Harvesting equipment employing nCoP plated hydraulic cylinder rods for enhanced corrosion resistance.

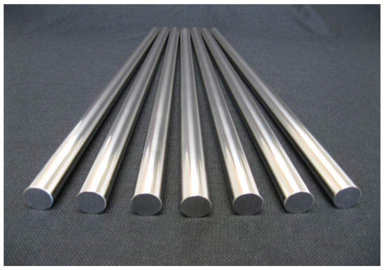

Figure 14: nCoP plated steel bars prior to machining and assembly.

CONCLUSION

Enduro Industries LLC has successfully implemented the nanostructured cobalt phosphorus (nCoP) process, an environmentally compliant alternative to EHC, for application to bar and tubing products used in the fluid power market. The nCoP exhibits superior corrosion, wear and fatigue performance compared to EHC. In future, Enduro plans to increase production capacity and fully automate process operations in order deliver a higher throughput while maintaining industry leading quality. Furthermore, Enduro plans to continue the development of specific fluid power market applications, expand the understanding of the process and its impact on commercialization, and continuously improve the production cell with an emphasis on expansion and automation.

For more information visit:
www.integran.com
www.chromerod.com

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