ELECTROLESS NICKEL SURFACE COATINGS APPLICATIONS AT CENOVUS ENERGY

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ABSTRACT

Electroless nickel coatings originated in 1943 at the U.S. Bureau of Standards. Follow-up research by scientists at General American Transportation Corp., Chicago, resulted in a commercial process for coating carbon steel caustic soda shipping drums. Today, electroless nickel coatings are used in a wide range of industries including: computers, automotive, aerospace, and oil & gas.

Electroless nickel coatings are only 25 to 100 microns (1 to 4 mils) thick. When properly applied these thin, uniform coatings have good bond strength and high surface hardness. Electroless nickel coatings are solution options for both erosive wear and corrosion. Since 2006, Cenovus has successfully utilized electroless nickel coatings in oilfield wellhead components. In 2011, Cenovus selected electroless nickel to address corrosion and erosion issues in pump casings at SAGD operations.

This paper provides basic information about electroless nickel coatings. The Cenovus experience with electroless nickel is described.

INTRODUCTION

Electroless nickel (**ENC**) is a family of coatings based on nickel-phosphorous metallic compounds. ENC was developed in 1943 by Abner Brenner, an electrochemist at the U.S. Bureau of Standards. While working on the electroplating of nickel onto nickel-tungsten surfaces, Brenner added hypophosphite chemical to the plating solution as a way to control surface oxidation. This addition increased the electric current efficiency, indicating the hypophosphite was promoting nickel deposition and supplementing the electroplating current. The research department of General American Transportation Corporation (GATC) built on Brenner's work and commercialized the "KANIGEN" ENC process in 1952. The term KANIGEN is derived as follows:

KA = catalytic, NI = nickel, GEN = generation

KANIGEN™ is a registered trademark used by licensed companies in Europe, U.S., and Asia. In today's global marketplace, KANIGEN™ is one of many ENC brands. ENC is available from at least three companies in western Canada. Innovative companies have developed new ENC products in response to customer needs. Examples include: ENC with industrial diamonds for abrasive applications, and ENC with PTFE particles to reduce friction.

Because electric current is not used in the ENC process, ENC is more uniform in thickness compared to traditional electroplated coatings. This is a desirable feature for coating complex shapes because edges and points can interrupt the electric current and cause uneven coating thickness.

ELECTROLESS NICKEL COATING 101

ENC is applied to prepared substrates by controlled immersion in a tank containing nickel and phosphorous chemical solutions. Carbon steel is the most common substrate, however, other substrates include: Cr-Mo steel, stainless steel, copper, aluminum, and even some plastics. The basic ENC procedure is outlined below:

1. Surface cleaning of substrate to remove grease.
2. Acid etching to remove mill scale and activate the surface to receive ENC.
3. Heat the ENC chemicals to 90°C.
4. ENC thickness is controlled by contact time with the ENC chemicals.
5. Post-coating heat treatment at 180°C to degass hydrogen from the ENC - substrate interface and improve bond adhesion.
6. Optional heat treatment at 300°C to 400°C to increase hardness.

Figure 1 shows details of the ENC tank. Tank sizes are selected to handle the size and shape of the coated part. Figure 2 shows a polished cross section of ENC on carbon steel; note the ENC conforms to the contour of the substrate.

The ENC process is similar to zinc hot dipped galvanizing. However, the corrosion mitigation is different. Galvanized zinc acts as a sacrificial anode to protect the carbon steel substrate. EN coatings are barrier layers preventing corrosion reactions on the substrate.

The ENC process involves two chemical reactions; an oxidation reaction which liberates electrons, and a reduction reaction which consumes electrons. The ENC process has these two key components:

1. Nickel sulphate: $NiSO_4(H_2O)_6$ → source of Ni^{2+} ions which are reduced to nickel metal on the substrate.
2. Sodium hypophosphite: NaH_2PO_2 → source of H to reduce Ni^{2+} ions at the substrate.

ENC chemical reactions proceed in these steps:

1. Diffusion of Ni^{2+} and $(H_2PO_2)^-$ ions on the surface
2. Adsorption of Ni^{2+} and $(H_2PO_2)^-$ ions on the surface
3. Chemical reactions at the surface:

Oxidation: $(H_2PO_2)^- + H_2O \rightarrow H^+ + (H_2PO_3)^{2-} + \mathbf{2H}$
Heat is applied to drive the reaction & generate H

Reduction: $Ni^{2+} + 2H \rightarrow \mathbf{Ni} + 2H^+$
H reduces Ni^{2+} to Ni metal on the surface

$(H_2PO_2)^- + H \rightarrow H^+ + H_2O + OH^- + \mathbf{P}$
P metal is a byproduct on the surface & dissolves into the Ni metal atomic lattice = ENC

$(H_2PO_2)^- + H_2O \rightarrow H^+ + (H_2PO_3)^{2-} + H_2$
Competing reaction generates H_2 gas at the surface

The competing $(H_2PO_2)^-$ reaction lowers the volume of H available to reduce Ni^{2+} to Ni metal. This makes ENC a low efficiency operation. Approximately 5 kg of sodium hypophosphite is required to reduce 1 kg of nickel sulphate.

Three grades of ENC are available. Grade is determined by Phosphorous content as follows:

Low Phosphorous ENC: 1 wt% P to 4.5 wt% P

Medium Phosphorous ENC: 5 wt% P to 10 wt% P

High Phosphorous ENC: 11 wt% P to 14 wt% P

Figure 3 is the Ni-Phosphorous phase diagram. The grades are represented by Greek letters: β is Low Phosphorous, γ is High Phosphorous, β + γ is Medium Phosphorous. The letter α represents the equilibrium concentration of 0.17 wt % P dissolved as solid solution in the Ni atomic lattice. At temperatures above 880°C, ENC degrades to a mixture of molten nickel phosphide, Ni_3P, and solid α. Ni_3P is an intermetallic phase. The service temperatures for ENC must be kept below the transition lines above the β, β + γ, and γ phase regions. The transition temperatures are established by the P content in the ENC. Low-P β is a "microcrystalline" structure; P atoms are solid solution dissolved in the nickel atomic lattice. Low-P β is slightly magnetic. High-P γ is an amorphous, non-crystal structure because the nickel atomic lattice is unable to dissolve the phosphorous atoms by solid solution. High-P γ is non-magnetic. The amorphous nature makes High-P γ an excellent coating for corrosion resistance because the lack of crystal structure reduces corrosion initiation sites. The amorphous structure also makes ENC immune to chloride stress corrosion cracking. Microcrystalline Low-P β has low corrosion resistance. However, it is much harder than High-P γ. This makes Low-P β a good choice for erosive wear applications. The Medium-P grade β + γ region in the phase diagram has an intermediate transition line at 250°C to 280°C. At temperatures above this line, the β phase is converted to α and this limits the usefulness of Medium-P ENC. In summary, the ENC grades for oil & gas applications are γ High-P ENC for corrosion resistance, and β Low-P ENC for wear resistance.

PROPERTIES OF ELECTROLESS NICKEL COATING

This paper focuses on four ENC properties which Cenovus considers to be essential. These properties are: adhesion, corrosion resistance, hardness, and wear resistance. A comprehensive overview of ENC properties is available in the referenced articles.

1) ADHESION

The bonds at the ENC – substrate are metallic and mechanical. Adhesion, which is a measure of the bond quality, is dependent on proper cleaning and pre-treatment of the surface. Bond strength between ENC and carbon steel is in the range 200 MPa to 420 MPa (29,000 psi to 61,000 psi). Bond strength (adhesion) is enhanced by post baking of the coating to degass residual hydrogen from the interface. The quality standard for adhesion is the bend test prescribed in ASTM B571 "Practice for Qualitative Adhesion Testing of Metallic Coatings"

2) CORROSION RESISTANCE

High-P ENC has excellent corrosion resistance in most environments, except caustic NaOH solutions at temperatures close to 100°C. The poor corrosion resistance is believed to be caused by leaching of phosphorous from the ENC by the hot caustic. Low-P ENC has better corrosion resistance for this caustic service.

High-P ENC has been successfully used in the oilfield since the 1980s. Table 1 summarizes the typical applications; most of these are in the U.S. Figure 5 presents corrosion rate data for Hi-P ENC handling salt brines with 20% CO_2 content and varying H_2S content. Temperature is an additional parameter. The Hi-P ENC performs well except for high H_2S levels above 65°C. Thus, ENC may have limited success for applications with H_2S.

Porosity is the major factor controlling ENC corrosion resistance. Corrosion will proceed if pores extend through the ENC to the substrate. Corrosion is accelerated by small anode area (carbon steel) to high cathode area (ENC) ratio at the bottom of the pores. Causes of porosity include: improper substrate cleaning, sloppy tank operation, trapping of H_2 at the substrate, and excessive surface roughness. Porosity is minimized by using thicker coatings. Lab studies have shown ENC thicker than 35 microns do not have pores connecting to the substrate. A possible explanation is additional Ni in thicker ENC is filling in pores which would have been present in thinner ENC.

3) HARDNESS

The hardness of ENC can be increased by heat treating at temperatures slightly above the transition line. Figure 4 relates hardness as a function of one hour heat treatment temperature for High-P ENC. Maximum hardness occurs at approx. 375°C. At this temperature, some β is transforming to intermetallic Ni_3P. The hardening mechanism is analogous to the precipitation hardening of 17-4 PH stainless steel. Some corrosion resistance of the High-P ENC is traded for improved wear resistance. The formation of intermetallic Ni_3P by hardening heat treatment can cause the ENC to shrink and lead to microcracking. If a pathway is opened to the substrate, corrosion will occur at high rate; the ENC will be cathodic to the exposed substrate. Hardening heat treatment of High-P ENC must be controlled prevent intermetallic Ni_3P and associated shrinkage and cracking.

4) WEAR RESISTANCE

Wear is defined as damage to a solid surface involving the progressive loss of material due to motion between the surface and a contacting substance. Three types of wear are typical in piping system pumps and valves. These are: abrasive wear, adhesion wear, and erosion wear. Abrasive wear is caused by hard particles forced against, and moving along a solid surface. Adhesive wear involves two events. High points on the surface are "cold welded" by an applied load when solids slide against each other. Tangential shearing breaks the cold welds which generates particles. Abrasive wear is more common than adhesive wear. Erosive wear is the third type and is the loss of material by particles and/or liquids impinging on the surface. The impinging energy breaks out particles. Erosion is the main wear mechanism in piping systems involving either slurry or two phase (liquid + vapour) flow.

Erosion wear resistance of ENC is difficult to measure. However, abrasive wear resistance is readily measured and used to infer erosion wear. The Taber Rotary Abraser (ASTM B773 Appendix X1) is used to measure abrasive wear. The Taber test involves an ENC sample rotating at fixed speed under two abrasive wheels. A 250 gram load is applied to each wheel. Worn particles are removed from the ENC sample by an attached vacuum. The Taber Wear Index (**TWI)** is the milligrams of ENC lost per 1,000 rotations. High TWI values indicate lower wear resistance. Lower TWIs indicate better wear resistance. Figure 6 shows TWI as a function of "as plated" ENC phosphorous level. Low-P ENC with TWI = 10 has better wear resistance compared to High-P ENC with TWI = 18. Although not indicated in Figure 7, heat treatment of High-P ENC to increase hardness will reduce the TWI. This will give the more corrosion resistant High-P ENC some measure of wear resistance.

Figure 6 shows the Falex Wear test on the right axis. This test, described in ASTM D2714, is used to evaluate adhesive wear. Notice how High-P ENC outperforms Low-P ENC on this scale. This is explained by the lower number of cold welds associated with the amorphous High-P ENC compared to the microcrystalline structure of Low-P ENC.

ELECTROLESS NICKEL COATING QUALITY

ASTM standard B733: "Specification for Autocatalytic (Electroless) Nickel – Phosphorous Coatings on Metal" is a comprehensive quality assurance guideline. Table 2 lists the quality assurance test references associated with ENC properties.

Phosphorous content in the ENC product can be measured by lab equipment such as: EDS spectrometry, X-Ray fluorescence spectrometry, and atomic absorption. Test coupons representative of the ENC coated part are used for the P content checks. Less sophisticated methods such as titration and dissolution in nitric acid are also utilized.

ENC thickness is confirmed by several methods including: micrometer gauging before and after coating, metallographic cross section, and weight gain on a test coupon.

Adhesion can be demonstrated by a bend test (ASTM B571). Figure 7 shows an accepted bend test of 50 micron thick Low-P ENC on Superduplex Zeron 100 substrate. Adhesion failure is visualized by delamination flaking of the ENC cause by the bend test.

ASTM B733 sec. 9.6 suggests several quantitative methods for checking ENC porosity. One method is immersion of an ENC test coupon coated (and heat treated if applicable) in a prepared ferroxyl solution. Ferroxyl consists of potassium ferricyanide and sodium chloride. After rinsing and drying, the surface is checked for blue spots which indicate porosity extends to the substrate surface.

ENC hardness is characterized by microhardness testing by ASTM B578. The Knoop diamond indenter penetrates to only half the depth compared to Vickers diamond indenter. The Knoop hardness scale is not as common as Vickers hardness scale. Knoop gives higher accuracy for thin, hard surfaces. Conversion charts published in ASTM E140 are used to convert between Knoop and the more common Vickers scales.

ELECTROLESS NICKEL COATINGS AT CENOVUS

The first ENC application by Cenovus was in 2006 for conventional oilfield wellheads and tubing with high corrosion rates. The ENC coatings have performed well and Cenovus continues with this application.

In August 2011, Cenovus utilized ENC to address corrosion in the casing of a disposal water pump at a SAGD facility. A corrosion assessment of this carbon steel multistage pump casing (Figure 8) was performed during scheduled maintenance. Figure 9 shows erosion corrosion on the internal channels of the top and bottom casing halves. The channel edges were restored to original thickness by welding build-up. A 50 micron (2 mils) thick layer of High-P ENC was applied to the casings for corrosion resistance. Figure 10 shows a close-up of the internal channels after ENC. Figure 11 is a bigger picture of the ENC casing. Note the semi-gloss finish of the High-P ENC. Because it is a dipping in tank process, the ENC coats all pump casing surfaces contacted by the plating solution. To maintain the required dimensional tolerances required for leak free sealing of the casings, the machined flange surfaces were not EN coated. This was accomplished by lacquer masking of the flange surfaces prior to tank dipping. Post ENC heat treatment to increase hardness was not performed to prevent the possibility of dimensional distortion of the casings. This pump has operated without problems since returning to service in October 2011. The performance of the ENC will be checked during the next maintenance rebuild which is expected in 2015. Monitoring the pump efficiency will also indicate the effectiveness of the ENC. High efficiency maintained up to the rebuild time can be attributed to the ENC preventing erosion corrosion of the internal channels.

Cenovus has selected ENC to deal with erosion corrosion in SAGD boiler valves. The boiler target is 80% steam quality; 80% is “dry steam” and 20% is “wet steam” droplets. At start-up, steam quality is below 80% and these valves send the off-spec steam to a holding pond. When 80% steam target is reached, the valves close to deliver the steam to the injection wells. Figure 12 shows a cross section of a corroded valve. The localized corrosion in the seat has opened a pathway for steam to bypass the fully closed valve. The rough appearance on the outlet channel compared to the inlet indicates bypassed steam is flashing and causing metal loss by cavitation erosion. The steam bypass reduces process efficiency. Corrosion through the valve body could ultimately cause a high pressure steam leak and safety risk. Cenovus tried Cr-Mo steel valve bodies in place of the carbon steel, however, these Cr-Mo steel valves also failed by the same corrosion/erosion mechanism. Higher alloys were also evaluated. Superduplex stainless steel was ruled out because the 300°C operating temperature is too close to the maximum service temperature limit set by ASME code for Superduplex materials. High nickel alloys such as Hastelloy C-276 or Alloy 59 are options. However, the valves are connected to the carbon steel piping by welding instead of flanges. This would require complex dissimilar metal welds. Cenovus will install two carbon steel valves with ENC as a solution to the erosion corrosion. One valve will feature Low-P ENC for erosion wear resistance, and one valve will feature High-P ENC for corrosion resistance. Operating performance will be monitored to establish the effectiveness of both coatings and determine which ENC grade to implement as the standard solution.

CONCLUSIONS

Electroless Nickel Coatings are a simple concept however, the complex electrochemistry required years of research to commercially develop ENC. Today, ENC is widely available and is a cost effective option for corrosive and wear applications. ENC is available in three different grades which require careful selection to achieve acceptable performance. The oil and gas industry relies on two grades: Low Phosphorous ENC for wear resistance, and High Phosphorus ENC for corrosion resistance. Medium Phosphorous ENC is utilized in other industries such as computers and decorative finishing.

ENC is limited to 325°C (approx.) service temperature to avoid phase composition changes which reduce corrosion resistance.

ENC is a high integrity coating achieved by rigorously controlled procedures supported by a quality assurance program.

Cenovus has over six years of successful ENC experience in oilfield wellheads. This ENC experience was expanded in 2011 to pumps at SAGD facilities. In 2012, Cenovus will utilize ENC to address corrosion and wear in high pressure steam bypass valves.

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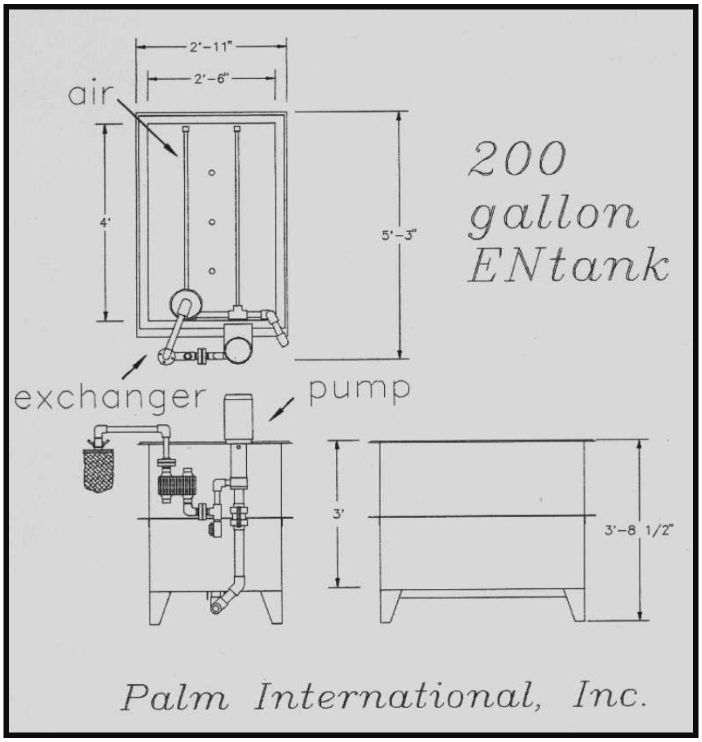
Table 1. Electroless Nickel Coatings – Oilfield Applications (source: reference 1)

Component	ENC Grade	ENC Thickness	ENC Function
Tubes	High P	50 – 100 µm (2 - 4 mils)	Corrosion & Wear
Pump casings	High P	50 – 75 µm (2 - 3 mils)	Corrosion & Wear
Sucker rods	High P	25 – 75 µm (1 - 3 mils)	Corrosion & Wear
Ball valves	High P	25 – 75 µm (1 - 3 mils)	Corrosion & Wear
Packers	High P	25 – 75 µm (1 - 3 mils)	Corrosion & Wear
Blow Out Preventers	High P	25 – 75 µm (1 - 3 mils)	Corrosion & Wear
Fire Tubes	High P	25 – 75 µm (1 - 3 mils)	Corrosion

Table 2. Key ENC Properties and Quality Assurance

PROPERTY	COMMENT	QA TEST REFERENCE
Phosphorous %	X-Ray Fluorescent, EDS Spectrometry, Atomic Absorption, wet chemistry	ASTM B733 sec. 9.1
Thickness	Micrometer gauging, Metallography, Weight gain	ASTM B733 sec. 9.3
Adhesion	Proper cleaning & preparation of substrate Optimize→ Bake @ 180°C to 200°C Bond Strength: 200 to 420 MPa (29 to 61 ksi)	ASTM B571: Bend test
Porosity	Ferroxyl test to reveal blue spot porosity	ASTM B733 sec. 9.6.1
Tensile Strength	Low P: 300 MPa (43 ksi) High P: 700 MPa (101 ksi)	ASTM C633
Ductility	Elongation to Fracture: 1 to 2.5% *brittle*	ASTM C633
Hardness HV=Vickers	Low P “as plated”: 600 HV to 700 HV High P “as plated”: 400 HV to 500 HV Hardness increased by heat treatment	ASTM B578 ASTM E140
Wear Resistance	Low P “as plated”: 8 to 10 Taber Wear Index Low P “heat treated”: 1 to 4 Taber Wear Index	ASTM B733 App X1 ASTM D4060
Thermal Expansion	12 to 14 µm/m/°C *similar to steel*	N/A
Magnetism	Low P: weakly magnetic High P: non magnetic	N/A

Figure 1. Electroless Nickel Coating Tank (source: Palm International)



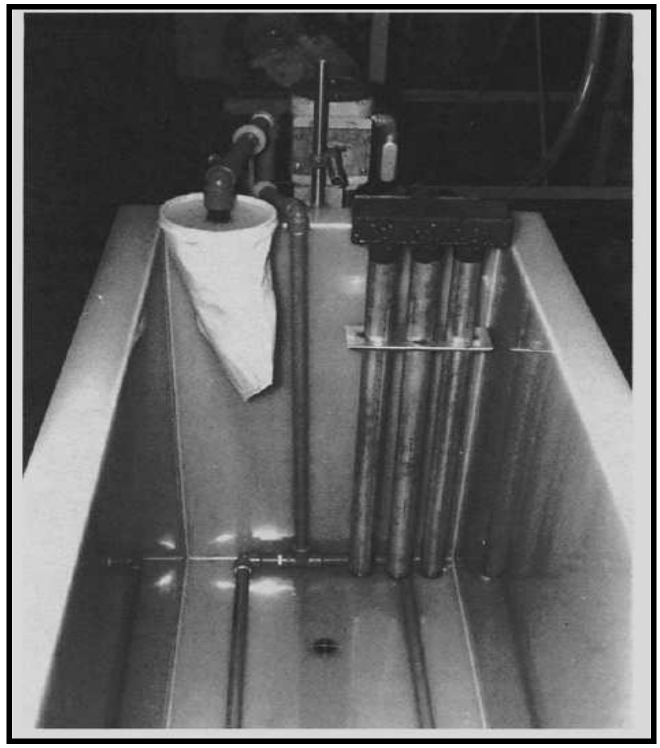


Figure 2. EN Coating on Carbon Steel (source: The Linden Group)

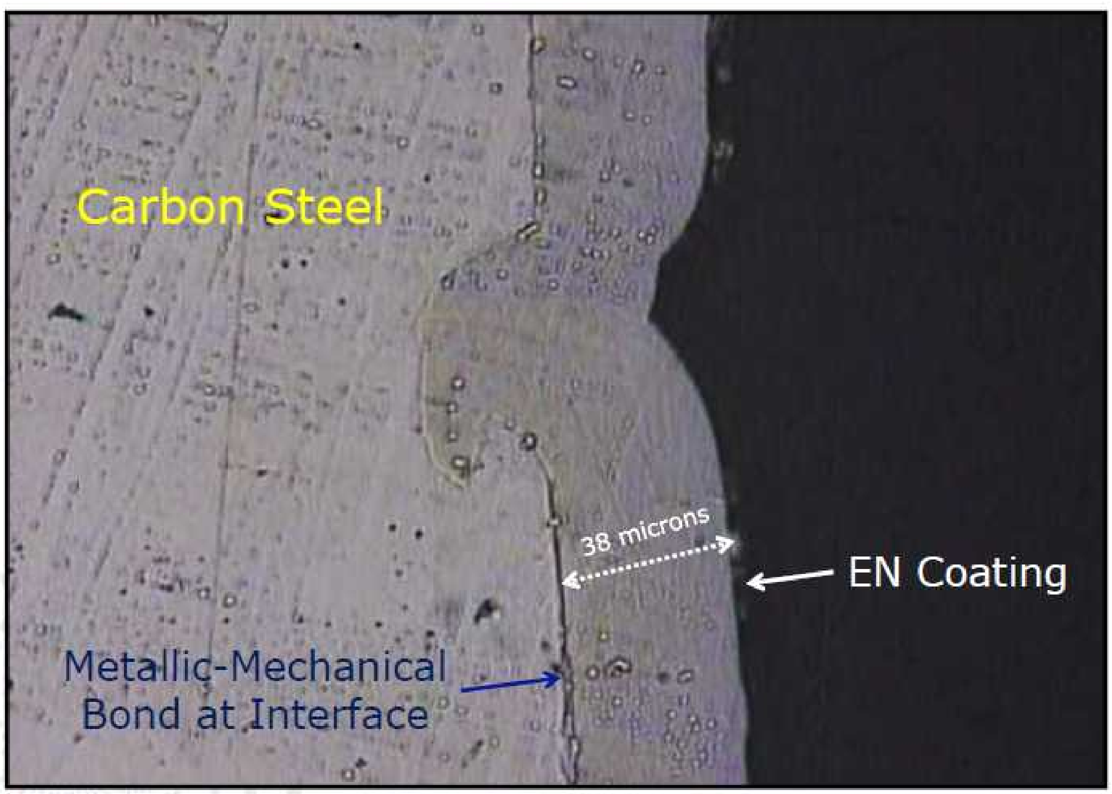


Figure 3. Nickel Phosphorous Phase Diagram (source: reference #5)

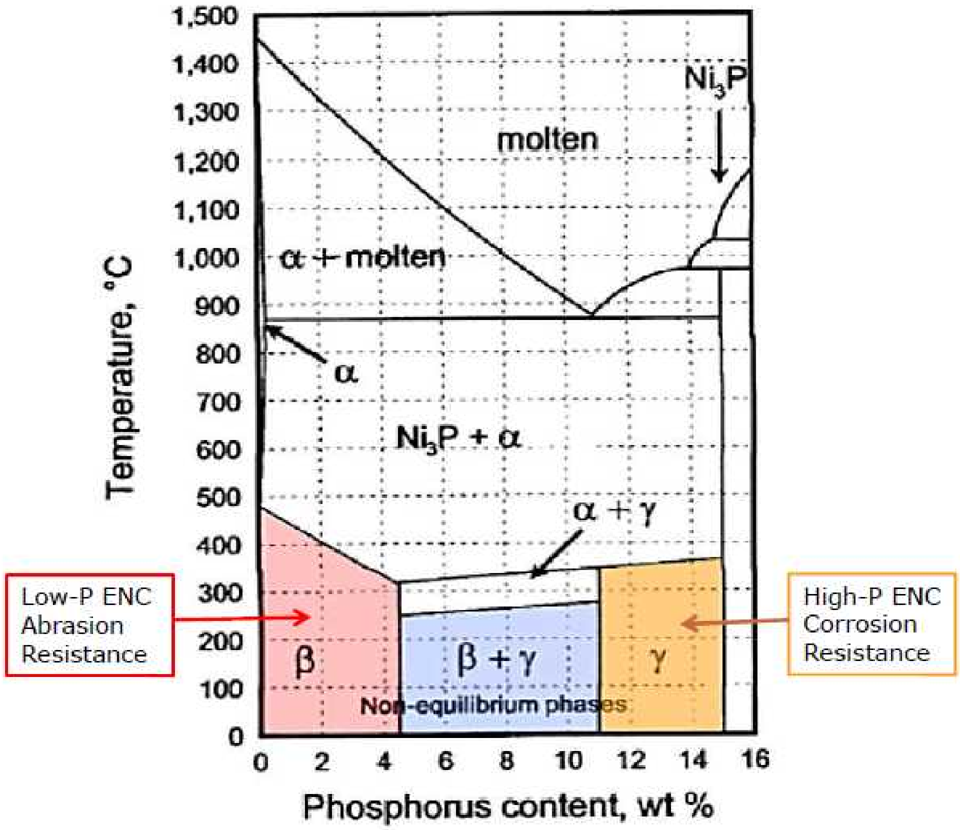


Figure 4. High-P ENC Heat Treatment to Increase Hardness (source: reference #5)

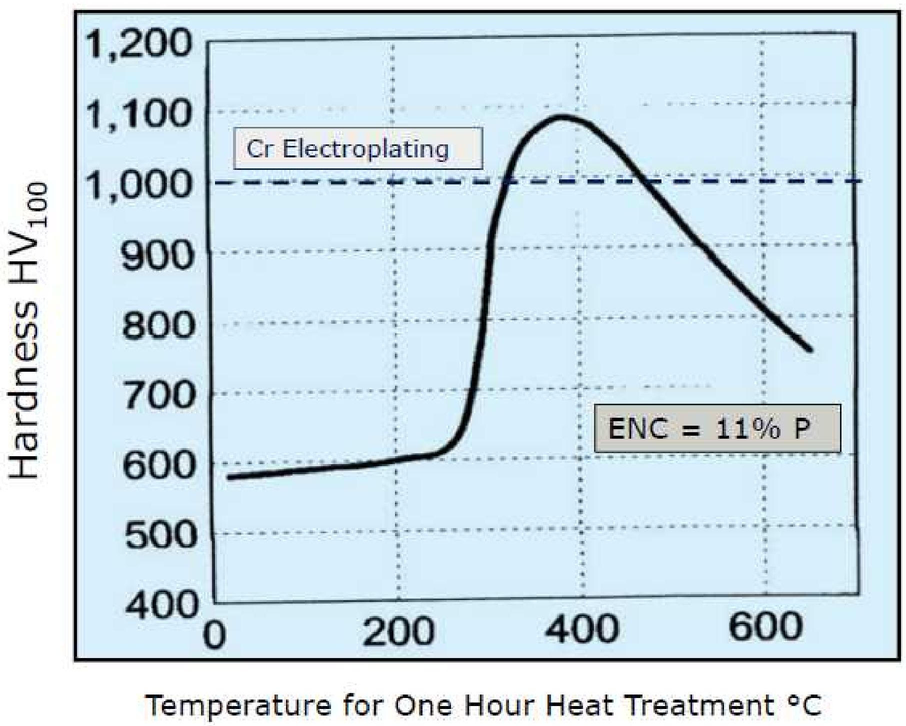


Figure 5. High-P ENC Corrosion Test Data (source: reference #5)

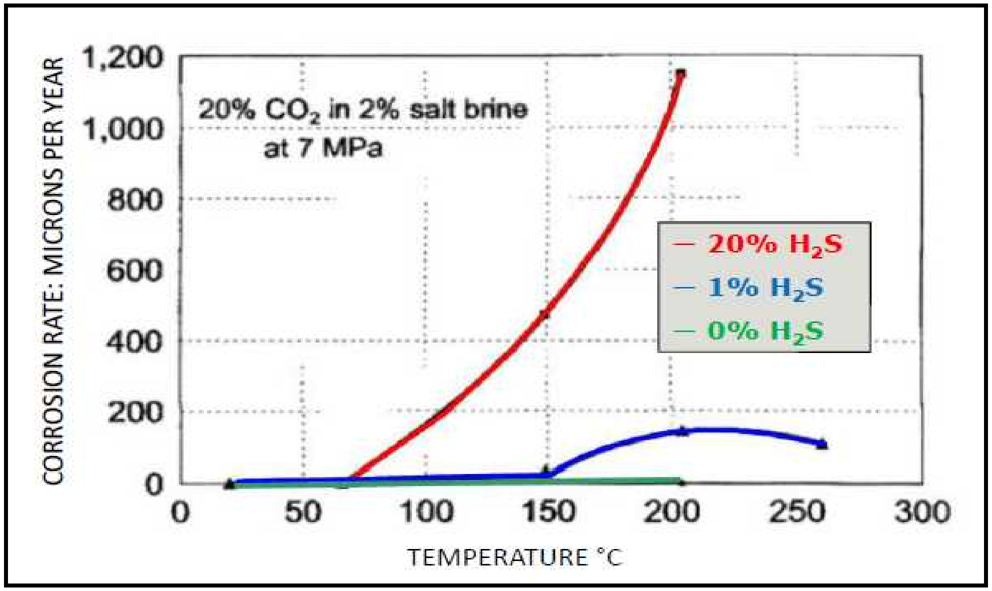


Figure 7. Bend Test

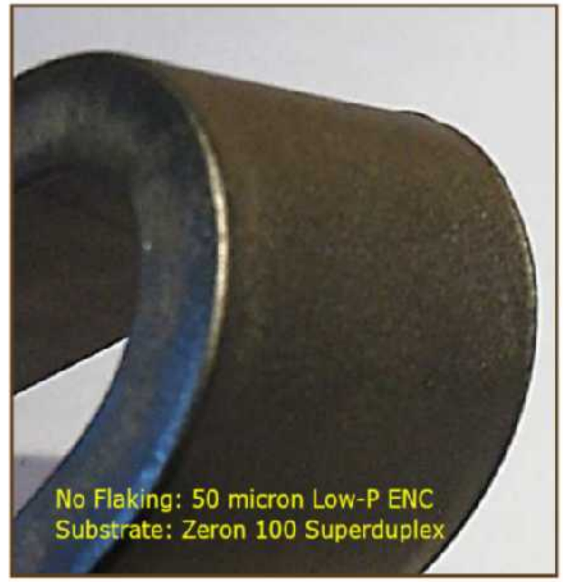


Figure 6. High-P ENC Wear Test Data (source: reference #5)

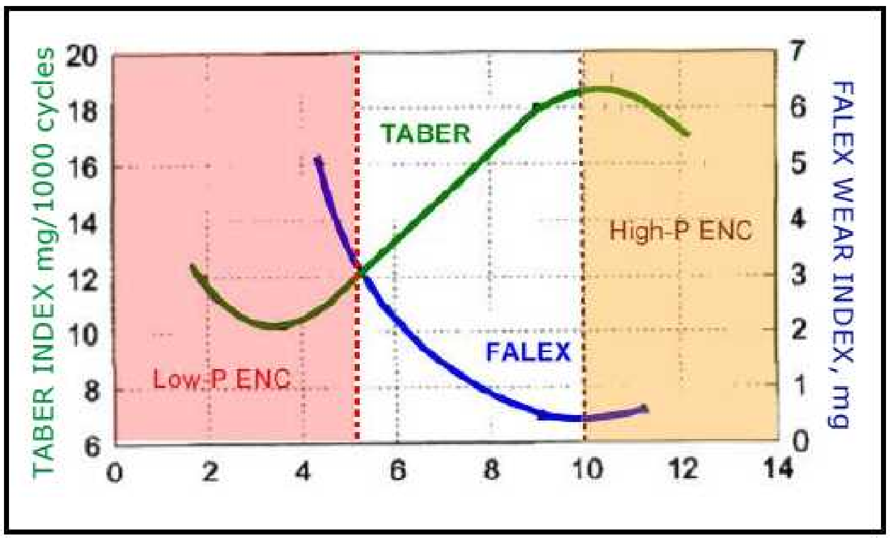


Figure 8. Cenovus Multistage Pump Casing Before ENC

Figure 9. Erosion Corrosion of Pump Internal Channels

Figure 10. High-P ENC on Pump Internal Channels

Figure 11. Pump Casing After High-P ENC

Figure 12. Steam Bypass Valve Cross Section