COMPARISON OF CORROSION/WEAR RESISTANT BARREL COATINGS AND THEIR FAILURE BEHAVIOR UNDER ACIDIC CONDITIONS

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ABSTRACT

Surface coatings are commonly used in many industries including oil and gas; with the aim of hardening the part surfaces to improve wear resistance without compromising the corrosion resistance -or even improve when applicable. Sucker rod pumps employ several parts with coated surfaces as well, including the pump barrels. Both standardized surface modifications and specialty applications for pump barrels are readily available in market for different well conditions, including extreme well solids and H_2S and CO_2 service. These service conditions can be detrimental for pump performance if the right coating is not used. In addition to service conditions, well treatment methods such as acidizing can also deteriorate the coating performance, causing pump failures. This study focuses on the structure of 6 different standardized and specialty coatings on sucker rod pump barrels and an experimental study on their degradation in acidic environments, while familiarizing the reader with the recommended service conditions.

INTRODUCTION

Surface modification in sucker rod pump barrels can be achieved through two main methods; methods that involve an intentional buildup or addition of a new layer (coatings and hardfacings), and the methods that involve surface and subsurface modification without any intentional buildup or increase in part dimensions (diffusion and selective hardening). The commercial barrel coatings that are studied in this paper are the ones that provide corrosion protection by forming a barrier between the corroding environment and the substrate. They do not have sacrificial ability as do cadmium or zinc deposits. Accordingly, the amount of porosity and cracking present in such coatings can greatly affect their corrosion protection ability of the base metal.

Hydrochloric acid (HCl) is commonly used in wells for acidizing treatment. The purpose being to stimulate the well to enhance diminished production. As much as being necessary for the well's production longevity, the treatment may damage some pump parts, including the coatings on the barrel. Chrome coatings, for example, are known to be very vulnerable to HCl attack. There are many other coatings, some API standardized and some not, in the market that aim to battle the harsh well conditions, as well as the acidizing jobs. API standardized Nickel Carbide (Ni-Carb) composite coating is one of these coatings, along with other specialized and proprietary ones.

The barrel coatings that are employed in this study are two API standardized Chrome coatings from different manufacturers (Chrome A and Chrome B), API standardized Nickel Carbide composite coating (Ni-Carb C), and three different specialty coatings (coating X, Y and Z). The HCl was introduced at higher concentrations than is usually found in the wells, except for the Chrome coating tests, for the sake of increased test rates. The details on the test setup and the results are given in the following chapters.

API Standardized Chrome Coating

Chrome plating, being the oldest and most common plating method employed to battle severe well and service conditions, is used to provide a very high degree of hardness on the surface of a metal to enhance wear resistance, reduce friction, provide anti-galling properties, and, in some cases, improve corrosion resistance. The coating, by nature, is porous and full of cracks, and formation of these cracks will increase as the coating thickness increases. The coating has poor resistance to acids; thus, the operator should pay extra attention to barrel selection if they are planning on acidizing the well.

Two different API standardized Chrome coatings are studied in this study, designated the Chrome A and the Chrome B. The properties of these two coatings are summarized in Table 1.

API Standardized Nickel Carbide Composite Coating

Nickel carbide composite coatings (Ni-Carb) are chemically applied on the base metal with suspended Silicon carbide (SiC) particles in a matrix of electroless nickel (EN). The hard particle electroless nickel composite coatings are widely used in oil and gas industry due to their excellent corrosion and wear resistance properties and ability to be applied uniformly on a variety of substrate materials and intricate part geometries. The dispersion strengthening effect of SiC particles and the strong Nickel Phosphorus (Ni-P) matrix enables such coatings to offer excellent wear resistance. The amount of SiC particles, the Phosphorus content of the matrix and heat treatment determine the mechanical and corrosion resistance properties of these deposits. The properties of the Ni-Carb coating used in this study (Ni-Carb C) are summarized in Table 2.

Specialty Barrel 1 (Coating X)

The manufacturer of this specialty barrel compared their product to Chrome coating. They claim that its hardness and wear resistance are comparable to Chrome, but their product outperforms due to the cracked nature of the Chrome coatings. It was also claimed that in HCl, their product is superior to Chrome coatings.

The laboratory tests and measurements on the Coating X yielded the results in Table 3.

Specialty Barrel 2 (Coating Y)

The manufacturer of this specialty barrel also compared their product to Chrome coating. They claimed that their coating exhibits excellent wear, corrosion, and chemical resistance compared to Chrome coatings. It was also claimed that Coating Y has superior corrosion resistance properties compared to Hard Chrome due to minimal, or lack of porosity, which results from a very dense, essentially amorphous deposit structure. The manufacturer also compares the HCl resistance of the barrel with that of Chrome and stated that “Coating Y has superior resistance to Hydrochloric acid solution. With acid solution levels as high as 15%, Coating Y had no visible reaction signs except for a slight discoloration on the surface.”

Specialty Barrel 3 (Coating Z)

According to the manufacturer, this specialty barrel is the same as Specialty Barrel 2, except that the coating is both on the ID and the OD of the barrel.

The laboratory tests and measurements on the Y and Z coatings yielded the results in Table 4.

TEST SETUP

The barrels of coatings to be tested are sectioned at around the central area for test piece extraction. The test pieces are masked such that there is a one square inch of the coated region exposed on the ID. 2.5% and 5% HCl solutions are prepared for the testing of Chrome A and Chrome B samples, and 15% HCl solution is prepared for the testing of Ni-Carb C, Coating X, Y and Z. Each experiment is performed three times to ensure the repeatability of the results. The experiment details are given in Table 5.

Once the designated times are reached, the specimens are pulled out of the solution and thoroughly rinsed. The exposed surfaces are documented. Then the metallographic samples are sectioned from the exposed specimens, mounted in epoxy and phenolic molds, and ground and polished according to ASTM E-3 Standard. Most of the samples are etched in 2% Nital solution to reveal the base metal microstructure. Axiovision software is used for quantitative measurements.

RESULTS AND DISCUSSION

The results of the acid exposure experiment can be discussed in three groups due to similarities of the structures of the constituents; the Chrome coatings (Chrome A and Chrome B), the electroless Nickel coatings (Coating Y and Coating Z), and the electroless nickel based composite coatings (Ni-Carb C and Coating X).

The results of the HCl exposure test for Chrome A and Chrome B coatings are summarized in Table 6. Chrome A did not show any signs of degradation under any test conditions given in Table 5. In fact, further testing revealed that degradation of Chrome A in 2.5% and 5% HCl started at 43 and 13 hours, respectively. Chrome B showed significant degradation in 2.5% HCl at 4 hours exposure, and the coating was fully dissolved in 5% HCl at the same time interval. 8 hours and 12 hours tests are not performed on Chrome B due to coating degradation and observed failure at 4 hours for both concentrations.

The Chrome coating is expected to undergo rapid corrosion attack when immersed in HCl. HCl reacts with Chrome, dissolving it with release of bubbles, a green salt, and leaving it dull. Chrome A and Chrome B both experienced the attack, but exhibited different resistances to the same test conditions, as shown in Table 6. This difference in corrosion resistance can be originated from the differences in the properties of the oxide layer on the deposit or the as-plated properties of the coating, mainly the presence of macrocracks, crack count, and plating process parameters.

The results of the HCl exposure test for Coating Y and Coating Z are summarized in Table 7. Both Coating Y and Coating Z exhibited signs of degradation at all acid exposure tests at 12, 24 and 48 hours. At 12 hours, both coatings revealed deep longitudinal cracks on their surface and the metallographic images of the deposits confirmed the presence of cracks. The acid solution reached the base metal and caused corrosion of the base metal even though the extent of the degradation is not evident on the coating surface. This type of degradation is especially dangerous since it does not give any signs on the part surface while the thickness of the base metal is steadily decreasing due to corrosion at crack locations. At 24 hours, the cracks are observed to form “ribbons” and started to come off from the deposit while the corrosion of the base metal is still taking place. At 48 hours, the coating is observed to be completely degraded.

Coating Y and Coating Z are medium-Phosphorus EN deposits, hardened to approximately 870 HV_{100} as stated in Table 4. The poor corrosion resistance of these alloys can be related to their post-heat treatment characteristics. According to as-plated Ni-P phase diagram in Figure 1, the deposit with 8% Phosphorus is a mixture of β-phase, a crystalline solid solution of P in Ni; and a fully amorphous γ-phase. In order to achieve a hardness of HV_{100} 870 (HVK 875), the deposit should be heat treated for 1 hour at around 360°C (Figure 2). Heating the part to this temperature will result in structural changes in the semi-crystalline deposit. First, at around 270°C, the beta phase converts to α-Ni, which results in precipitation of fine particles throughout the deposit. When the temperature is increased to 320°C, γ phase and any β which may remain under non-equilibrium conditions converts to Ni_3P and α-nickel, resulting in a crystalline deposit. Amorphous EN deposits are more resistant to corrosion due to their homogeneous structure and the absence of grain boundaries, dislocations, kink sites and other surface defects [3]. Accordingly, the corrosion resistance of the deposit will decrease when the deposit begins to crystallize and lose its amorphous structure.

Formation of Ni_3P in the deposit reduces the elemental phosphorus content in the bulk of the deposit and the coating’s corrosion resistance is therefore reduced (Figure 3). Ni_3P particles further contribute to the deposit’s destruction by creating active/passive corrosion cells.

In addition to these, the cracking of the deposit due to shrinkage and stresses that form during heat treatment also degrades the properties of the deposit. In the current study, the effects of this degradation were observed in two main features. First, the cracks that went through the entire depth of the deposit exposed the base metal to direct corrosion attack (Figure 4 (a)). Second, the cracks that did not reach the base metal and run parallel are observed to join and form “ribbons” (Figure 4(b)). These ribbons come off and may cause spalling in tight tolerances.

The results of the HCl exposure test for Ni-Carb C and Coating X are summarized in Table 8. Neither electroless Nickel based composite coatings exhibited any signs of degradation at the test conditions at 12 hours of exposure. The metallographic studies also verified intact coatings without any signs of corrosion. One of each three 24 hours exposure test pieces from both Ni-Carb C and Coating X exhibited physical separation of the coating during sectioning for metallographic specimen preparation, despite showing no evidence of failure on the test piece. The remaining two samples of each group remained undamaged during metallographic specimen preparation, but the microscopic analysis revealed degradation at the base metal-coating interfaces. Regardless, Ni-Carb C and Coating X showed the best corrosion resistance performance to the test conditions. The improved corrosion resistance compared to electroless Nickel coatings (Coating Y and Coating Z) can be attributed to the higher Phosphorus content of the matrix (Figure 5), and the post-plating heat treatment utilized on the deposit. Both Ni-Carb C and Coating X matrices are high-Phosphorus electroless Nickel, with 11% Phosphorus. According to the as-plated Ni-P phase diagram given in Figure 1, the matrix with 11% Phosphorus consists purely of the fully amorphous γ-phase. The coating does not need to possess a very high hardness to have a comparable wear resistance to Chrome coating, due to the improvement from very hard SiC particles embedded in the coating. The heat treatment that is applied to the coating is for Hydrogen relief [4] and does not cause any phase transformation, leaving the matrix in its amorphous state. The negative effects that are associated with high temperature post-plating heat treatment of electroless Nickel discussed in the previous chapter are not observed in Ni-Carb C and Coating X and thus the better HCl corrosion resistance is observed.

The most significant differences between the two coatings on the ID of the barrels are in particle density and coating thickness. The higher particle density of Coating X compared to Ni-Carb C is anticipated to result in improved wear resistance [5], but it did not prove to have a significant effect on HCl corrosion resistance of the coating in this study. The coating thickness also did not show appear to have a significant effect on corrosion resistance. The flaking off from both coatings at 48 hours can be attributed to the alterations in the plating bath chemistry for accommodation of the incorporation of the SiC particles. In addition, the expected improvement in adhesion by interdiffusion during heat treatment is not fully experienced due to the lower temperatures employed during the post-plating heat treatment of the deposit.

CONCLUSION

This study focused on the structure of six different barrier coatings that are industrially deposited on sucker rod pump barrels and the results of an experimental study on their degradation in HCl acid environments. Studying the results, the following conclusions were drawn:

- As verified by many case studies and data in literature, Chrome coatings have very low resistance to HCl exposure. Regardless, not all the Chrome coatings perform the same under these conditions. Quality of the Chrome coatings in the sucker rod pump manufacturing industry are very different from each other.
- Electroless Nickel coatings are heat treated at higher temperatures to have comparable hardness and wear resistance to Chrome coatings. This high temperature heat treatment results in decrease in corrosion resistance through loss of amorphous structure, formation of small corrosion cells, and macrocracks that expose the base metal.
- Electroless Nickel based composite coatings exhibit the best corrosion resistance to HCl solution in the test group. The SiC particle density and coating thickness did not have a significant effect on corrosion resistance in this test group.

REFERENCES

[1] Duncan, R.N., The Metallurgical Structure of Electroless Nickel Deposits: Effect on Coating Properties, 1996

[2] Parkinson, R., Properties and applications of electroless nickel, Nickel Development Institute

[3] Raicheff R., Zaprianova V., Effect of crystallization on the electrochemical corrosion behavior of some nickel-based amorphous alloys, 2000

[4] Electroless Nickel Coatings, NACE International Publications, 1997

[5] Sudagar, J., Lian, J., Sha, W., Electroless nickel, alloy, composite and nano coatings – A critical review, Journal of Alloys and Compounds, 2013

Table 1. Properties of Chrome A and Chrome B.

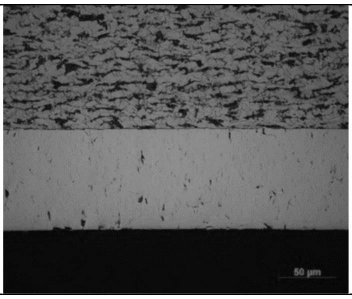
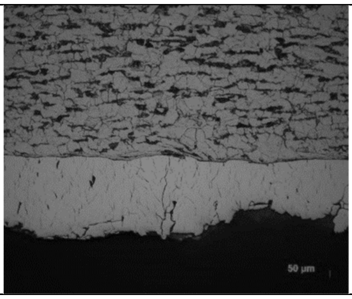
	Chrome A	Chrome B	API 11AX Specification
Coating Thickness	101.4 microns	64.4 microns	76.0 microns minimum
Coating Hardness (HV_{100})	1046.7	926.0	900-1160
Structure	Electroplated hard Chrome only on ID	Electroplated hard Chrome only on ID, nodular surface, macrocracks	N/A
			N/A

Table 2. Properties of Ni-Carb C.

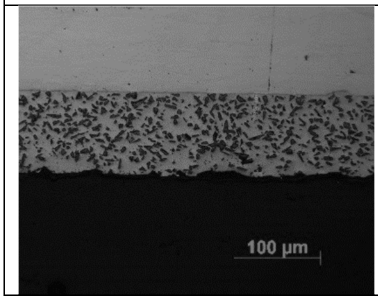
	Ni-Carb C		API 11AX Specification
Coating Thickness	95.5 microns		76.0 microns minimum
Coating Hardness (HV_{100})	672.3		N/A
Structure	Electroless Ni-P deposit with SiC particles, both on OD and ID		N/A
	Matrix	11.0%P 89.0%Ni	N/A
	Particles	18.1%C 81.9%Si	N/A
	Particle Density (%)	35	N/A

Table 3. Properties of Coating X.

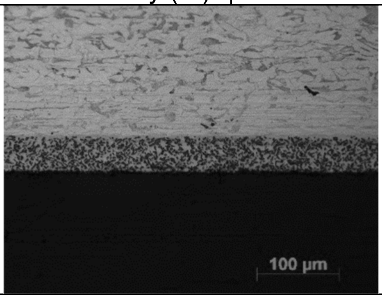
	Coating X Tests and Measurements		Manufacturer Claim
Coating Thickness	44.9 microns		N/A
Coating Hardness (HV_{100})	664.8		1128
Structure	Electroless Ni-P deposit with SiC particles only on ID		Comparable to Chrome coating, more uniform
	Matrix	10.6%P 89.4%Ni	N/A
	Particles	19.6%C 80.4%Si	N/A
	Particle Density (%)	47	N/A
			N/A

Table 4. Properties of Coating Y and Coating Z.

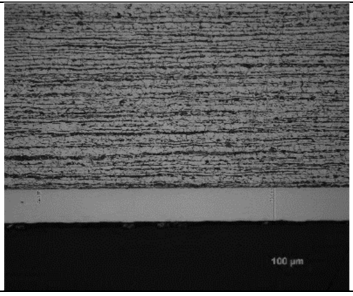
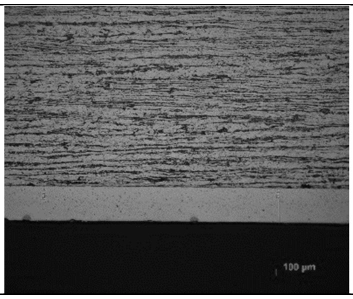
	Coating Y Tests and Measurements	Coating Z Tests and Measurements		Manufacturer Claim
		ID	OD	
Coating Thickness	71.9 microns	75.7 microns	98.2 microns	0.003 in minimum
Coating Hardness (HV_{100})	846.4	886.3	858.7	Meets API hardness requirement
Structure	Electroless Ni-P deposit 7.9%P, 92.1%Ni	Electroless Ni-P deposit		Comparable to Chrome coating, more uniform
				

Table 5. HCl exposure test conditions.

	Chrome A			Chrome B			Ni-Carb C			Coating X			Coating Y			Coating Z		
HCl Test Solution	2.5%		5%	2.5%		5%	15%			15%			15%			15%		
Test Time (hrs)	4	8	12	12	24	48	12	24	48	12	24	48	12	24	48	12	24	48

Table 6. HCl exposure test results for Chrome A and Chrome B.

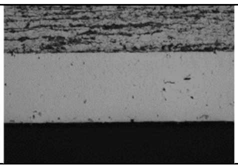
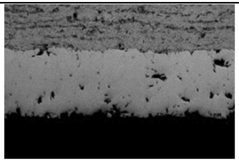
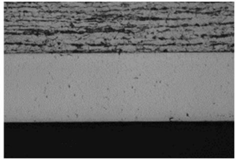
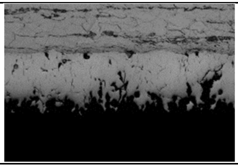
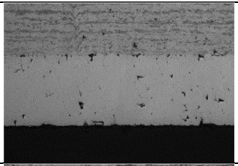
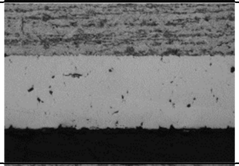
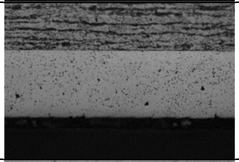
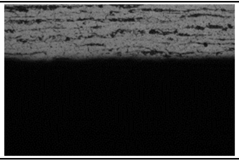
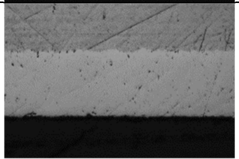
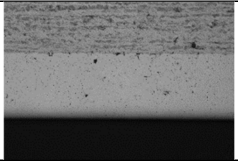
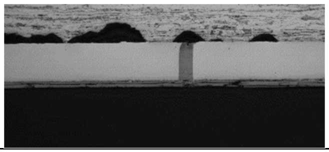
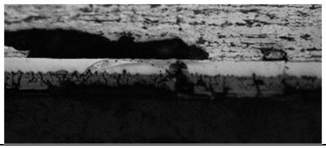
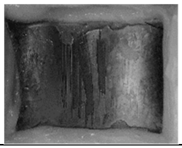
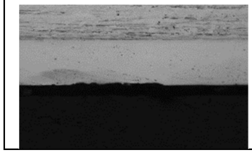
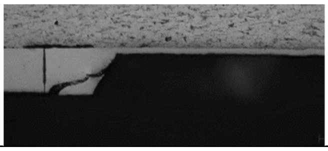
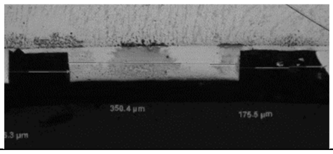
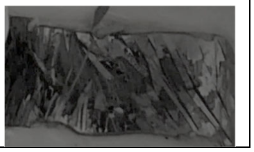
		Chrome A		Chrome B	
Unexposed					
2.5% HCl	4 hours		No degradation		Coating started dissolving
	8 hours		No degradation	N/A	
	12 hours		No degradation	N/A	
5% HCl	4 hours		No degradation		Coating fully dissolved
	8 hours		No degradation	N/A	
	12 hours		No degradation	N/A	

Table 7. HCl exposure test results for Coating Y and Coating Z.

Unexposed	12 hours	24 hours	48 hours
Coating Y 	Longitudinal cracks form, creep corrosion observed in some samples. Layer separation observed in some samples. 	Severe creep corrosion, severe "ribbon" flaking observed. Layer separation observed in some samples. 	"Ribbon" flaking observed 
Coating Z 	Longitudinal cracks form, creep corrosion observed in some samples. Layer separation observed in some samples. 	Severe creep corrosion, severe "ribbon" flaking observed. Layer separation observed in some samples. 	"Ribbon" flaking observed 

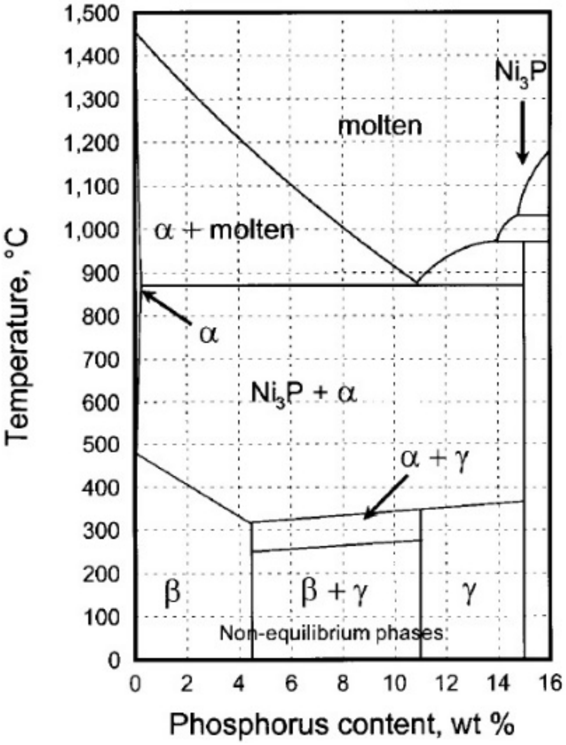


Figure 1. As-plated Ni-P phase diagram. [1]

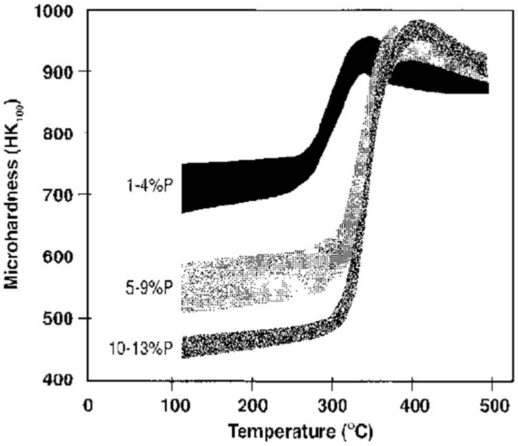


Figure 2. Effect of one-hour heat treatment and Phosphorus content on hardness of Ni-P deposit. [2]

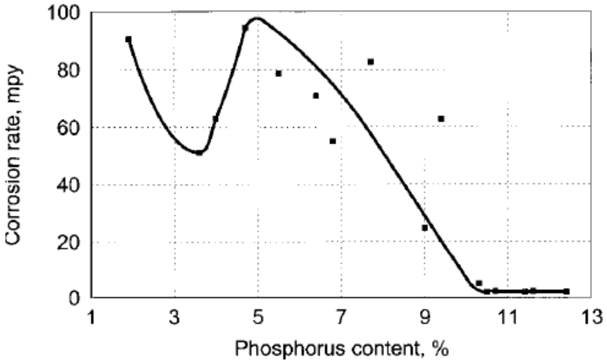
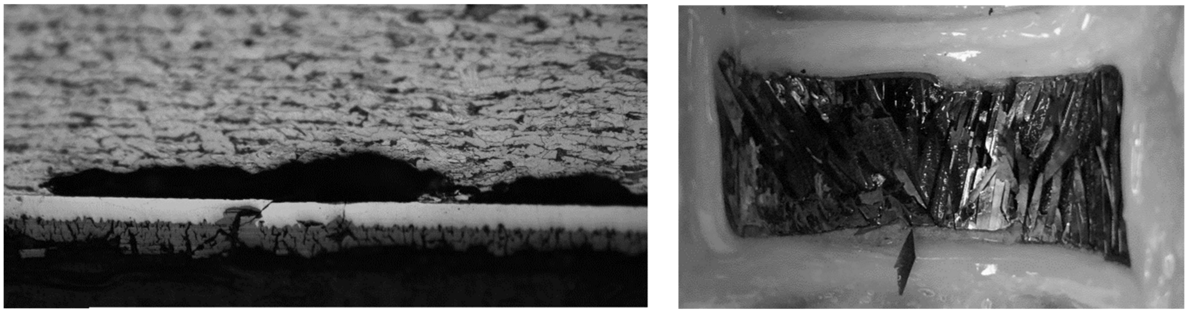


Figure 3. Effect of Phosphorus content on the corrosion of Electroless Nickel coatings in 10% HCl Acid Solution. [4]

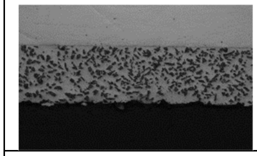
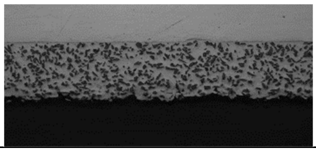
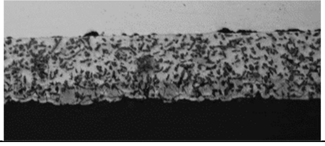
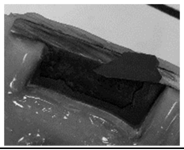
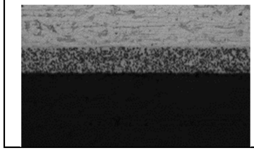
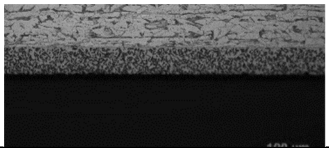
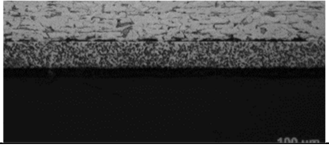


(a)

(b)

Figure 4. (a) Direct corrosion attack on the base metal due to heat treatment shrinkage crack after 24 hours of HCl exposure. (b) “Ribbons” coming off from the deposit after 48 hours of HCl exposure.

Table 8. HCl exposure test results for Ni-Carb C and Coating X.

Unexposed	12 hours	24 hours	48 hours
Ni-Carb C 	No degradation 	Coating started separating from base metal in some samples 	Coating physically separated 
Coating X 	No degradation 	Coating started separating from base metal in some samples 	Coating physically separated