



Electrodeposition of Nanocrystalline Cobalt Phosphorous Coatings as a Hard Chrome Alternative

Ruben A. Prado, CEF
Inorganic Coatings SME

NAVAIR Jacksonville
Phone: (904) 790-6381
Email: ruben.prado@navy.mil

18 - 20 Nov 2014



Report Documentation Page

*Form Approved
OMB No. 0704-0188*

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1. REPORT DATE NOV 2014	2. REPORT TYPE	3. DATES COVERED 00-00-2014 to 00-00-2014			
4. TITLE AND SUBTITLE Electrodeposition of Nanocrystalline Cobalt Phosphorous Coatings as a Hard Chrome Alternative		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Systems Command, Jacksonville, FL, 32202		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES ASETSDefense 2014: Sustainable Surface Engineering for Aerospace and Defense, 18-20 Nov 2014, Fort Myer, VA.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 35	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			



Project Team

NAVAIR: NAV  AIR

- PI: Ruben Prado, NAVAIR JAX
- Co-PI: Jack Benfer, NAVAIR JAX



Robert Kestler	<i>NAVAIR CP - Requirements and Demonstrations across NAVAIR programs and OEM</i>
Mike Firth	<i>NAVAIR LK - Ground Support Equipment requirements and components</i>
Steve Brown	<i>NAVAIR PAX - Test requirements and Qualification, JTP</i>
Denise Aylor	<i>NAVSEA - Leveraged Effort, NAVSEA Systems Requirements, Mil-Spec development</i>

Integran Technologies:



- Neil Mahalanobis, Constantine Collias
Integran – *Technology Development & Optimization, Dem/Plan*
- Keith Legg, Rowan Technology Group, Libertyville, IL, -- *CBA, reports, Implementation Assessment, ASETSDefense website*



Technical Objectives

- **Demonstrate/Validate pulsed electrodeposition of Nanocrystalline Cobalt-Phosphorous (nCoP) alloy coatings as a Hard Chrome (EHC) electroplating alternative for DoD manufacturing and repair.**
 - Fully define deposition parameters and properties
 - Establish production plating processes (i.e., cleaning, racking, masking, activation, pre-plates, stripping, etc.)
 - Demonstrate/Validate performance
 - Develop Eng Tech Data Packages
 - Manuals
 - Specifications
 - Eng. Circular
 - Transition Package
 - Initiate DoD and OEM approval process



Demo Site: FRC JAX



Technology Description

(nCoP Pulsed Electrodeposition)

Coating applied by electrodeposition

- Pulsed Current Waveform Engineering
 - Frequency (Hz) = $1/(t_{on}+t_{off}) = 25\text{Hz}$
 - Duty Cycle (%) = $t_{on}/(t_{on}+t_{off}) \times 100 = 50\%$



Electrodeposited nanocrystalline materials

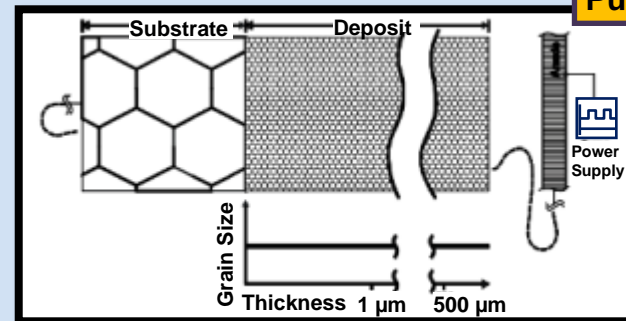
- *Favors nucleation of new grains over growth
- Results in an ultra-fine grain structure
- Uniform throughout thickness

Leads to unique properties

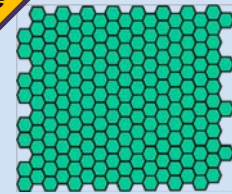
- ↑ Yield Strength, wear, ultimate tensile strength
- ↑ Density
- ↓ Coefficient of friction

*Smaller grain size impedes dislocation movement and increases yield strength

Nanocrystalline Electrodeposit



Pulse

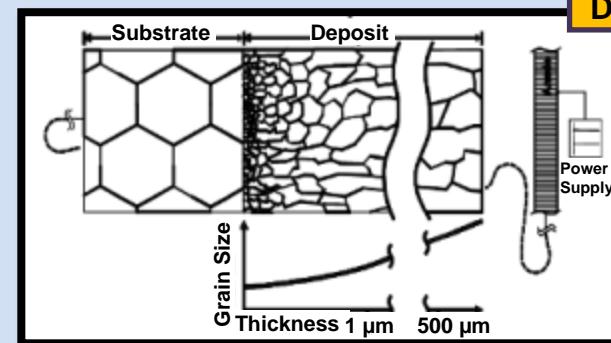


*Nanocrystalline
($< 100\text{ nm}$)

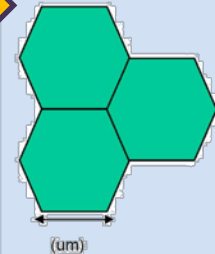
116 ASF, 50%, 25 Hz

*nCoP electrodeposits have grains of $\leq 20\text{ nm}$;
(hexagonal close-packed (HCP) crystal structure)

Conventional Electrodeposit



DC



Polycrystalline
(10-100 μm)



Technology Description

(nCoP Pulsed Electrodeposition)

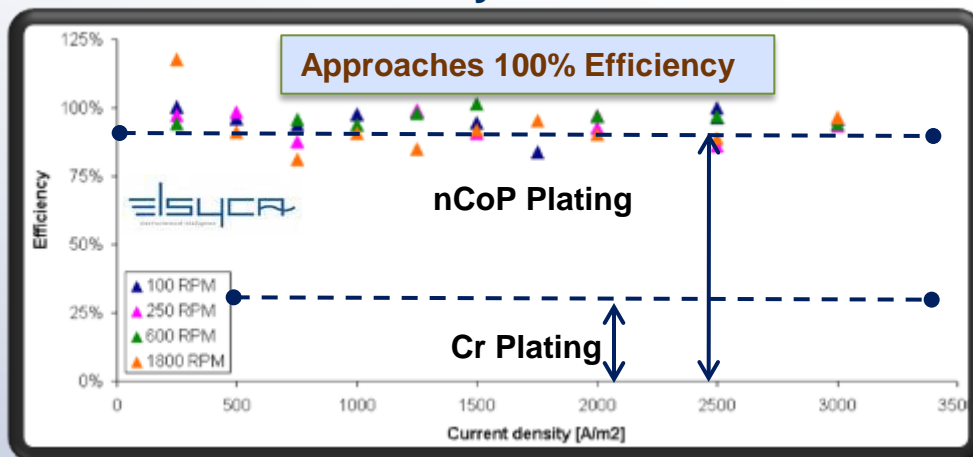
Process Comparison

	Nanovate™ R3010	EHC
Deposition Method	Electrodeposition (Pulse)	Electrodeposition (DC)
Part Geometries	LOS and NLOS	LOS and NLOS
Efficiency	85-95%	15-35%
Deposition Rate	0.002"-0.008" /hr	0.0005"-0.001" /hr
Emission Analysis	*Below OSHA limits	Cr+6
Bath Temperature	185°F	140°F



*Co PEL is 20 µg/m3

Cathode Efficiency



Nanovate™ R3010 Plating Tank at FRCSE
 Temp = 185°F
 pH = 1.0 – 1.2

- At least 5X faster than Chrome plating
- Increased throughput
- One nCo-P tank can replace several hard chrome tanks
- Bath is Stable



Technical Approach

(Dem/Val Line at FRCSE- Jacksonville)

■ NAVAIR Fleet Readiness Center Jacksonville

- Dem/Val line in operation since 2006
- 250 gallon Plating Tank
- Pulse Power supply (1500A Peak Current)
- Activation tank used for most all alloys
- CIP # 0466 Established



Process Line



Dem/Val Tank Pulse Power Supply

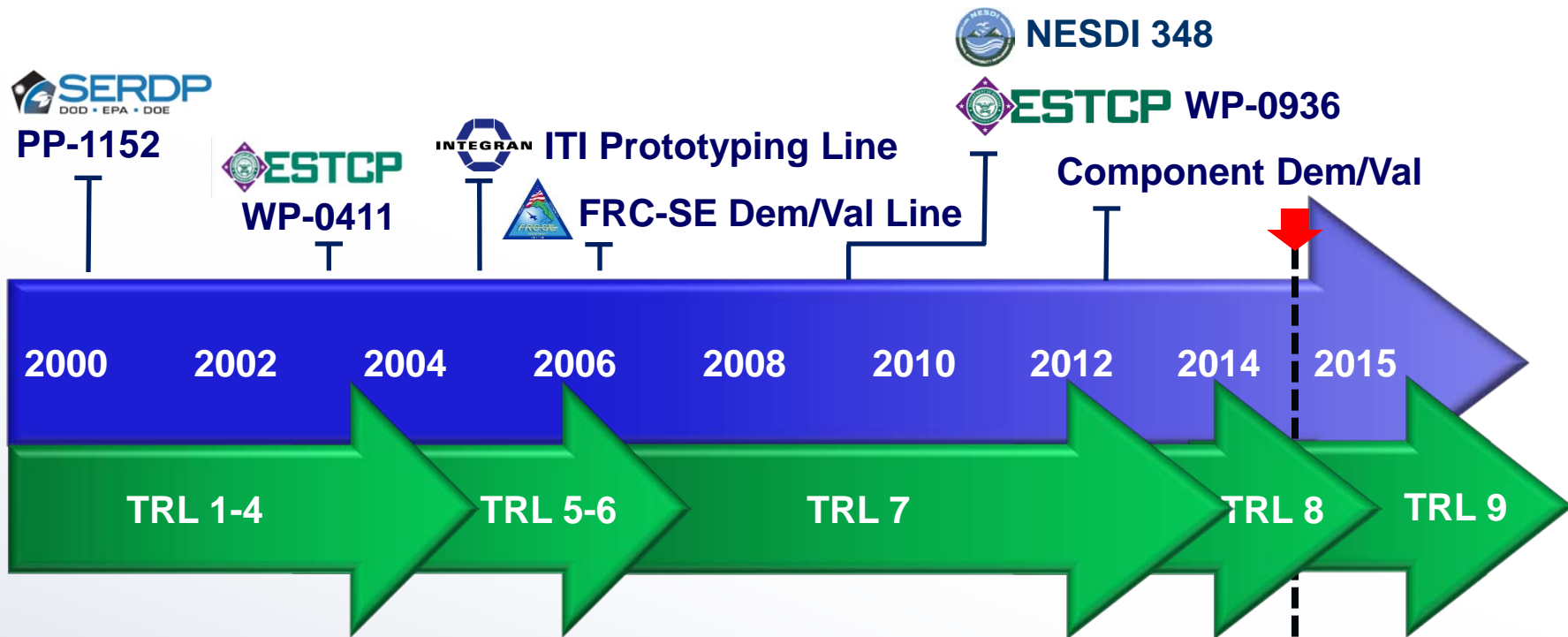


Activation Tank Power Supply



Technology Integration

(Technology Readiness Level)



COMFRC Technology Investment IPT is addressing technology integration priorities with NAVAIR HQ Compliance Group





Joint Test Protocol

(JTP - Demonstration/Validation)

24 Core Tests Defined in JTP

3 Dem/Vals

- | | |
|-------------------------|----------------------------|
| 1. Appearance ✓ | 13. Corrosion (OCP) ✓ |
| 2. Thickness ✓ | 14. Adhesion ✓ |
| 3. Porosity ✓ | 15. HE ✓ |
| 4. Hardness ✓ | 16. HE (No Bake) ✓ |
| 5. Grain Size ✓ | 17. Fluid Compatibility ✓ |
| 6. Ductility ✓ | 18. HRE ✓ |
| 7. Stress ✓ | 19. Wear - Taber ✓ |
| 8. Fatigue ✓ | 20. Wear - Pin on Disk ✓ |
| 9. Coating Integrity ✓ | 21. Wear - Endurance Rig ✓ |
| 10. Corrosion (B117) ✓ | 22. Wear - Falex ✓ |
| 11. Corrosion (SO2) ✓ | 23. Wear - Gravelometry ✓ |
| 12. Corrosion (Beach) ✓ | 24. Wear - SATEC ✓ |



T45 Pivot
Installed: Mar 2012



Lifting Arm Pin
Installed: Jul 2013



M9ACE Cylinder
Installed: Mar 2014

- 100 % Plating/Testing completed
- 100% Draft JTR completed
- 95% Dem/Vals Completed



Performance Criteria/Results

(Joint Test Protocol - Demonstration/Validation)

Engineering Requirement	Test	Acceptance Criteria / Notes	Results
Appearance	Visual examination	Smooth, fine grained, adherent, uniform in appearance, free from blisters, pits, nodules, excessive edge build-up and other defects	Pass
Porosity	Ferroxyl	No pits > 1/32" diameter < 15 pits in 150 sq.in < 5 pits in 30 sq.in.	Pass
Hardness	Vicker's microhardness	Hardness: nCoP ≥ EHC	Pass on selected heat treatment conditions
		Target Hardness > 850 VHN (EHC requirement) nCoP maximum hardness obtained 763 VHN following heat treatment 550°F for 5 hrs.	Fail
		Threshold Hardness > 530 VHN (process requirement)	Pass
Fatigue	Axial Fatigue	S-N curve fitted data: nCoP ≥ EHC at 0.003"	Pass
		S-N curve fitted data: nCoP ≥ EHC at 0.010"	Pass
		S-N curve data fitted: nCoP at 0.010" ≥ Ni+EHC at 0.005" ≥ Ni+nCoP at 0.005"	Marginal Pass



Performance Criteria/Results

(Joint Test Protocol - Demonstration/Validation)

Engineering Requirement	Test	Acceptance Criteria / Notes	Results
Coating integrity	Axial fatigue	The nCoP coatings must not spall or delaminate	Pass
Corrosion	<ul style="list-style-type: none"> SO₂ salt fog Beach exposure Neutral Salt Fog 	Average appearance/Protection ranking vs time curve: nCoP ≥ EHC per ASTM B537	Pass
Corrosion	Open circuit potential	No acceptance criteria – for information purposes only	Pass
Adhesion	Bend/chisel ASTM B571 AMS 2460	nCoP does not show separation from the basis metal at the common interface	Pass
Hydrogen embrittlement	<ul style="list-style-type: none"> Bake No Bake 	1a1: four bars > 200h load to failure: nCoP ≥ EHC	Pass
Environmental Embrittlement	Sustained load in saltwater environment	150 hrs+ and 45% NFS+: nCoP ≥ EHC in DI water nCoP ≥ EHC in Salt water	Pass (DI water)
Fluid compatibility	Visual observation and weight loss following immersion	nCoP must not exhibit chemical attack greater than that exhibited by EHC.	Pass
			Fails with Chlorine Bleach, Nital Etch & Ammonium Persulfate



Performance Criteria/Results

(Joint Test Protocol - Demonstration/Validation)

Engineering Requirement	Test	Acceptance Criteria / Notes	Results
Wear	Pin on disk	Coating wear volume loss, coefficient of friction, static partner wear volume loss: nCoP ≤ EHC	Pass
	Endurance rig test	< one drop of hydraulic fluid in 25 cycles and acceptable wear (i.e., not affecting leakage performance)	Pass
	Falex block on ring	Coefficient of friction, average weight loss and average wear volume: nCoP ≤ EHC	Pass
	Gravelometry	CoP performance equal to EHC	Pass
	Taber Abrasion	Taber wear index: nCoP ≥ EHC	Fail
	SATEC oscillating load	Coefficient of friction, average bushing wear: nCoP ≤ EHC	Pass

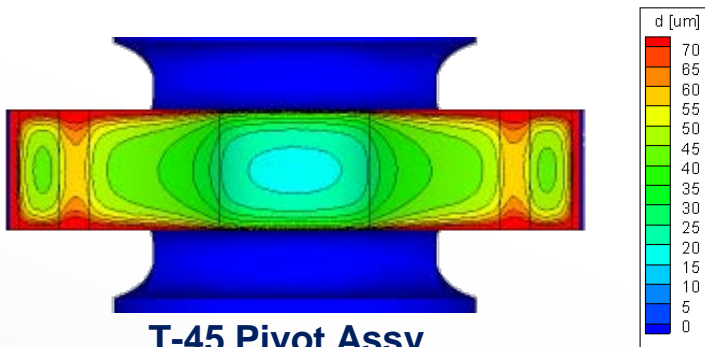


Technical Progress

(Overview of Prior Work)



Electrochemical Modeling



T-45 Pivot Assy



Phase I Characterization (JTP) Tests

	Requirement	nCoP	EHC
Appearance	Smooth, uniform, free of pits/defects	Pass Bright & shiny	Pass Dull/Matte
Adhesion	No separation between deposit/substrate	Pass	Pass
Ductility	> 2%	Pass 2.9%	Pass <1.0%
Grain Size	<20 nm (HCP)	Pass 6 nm(HCP)	N/A
Porosity	<1/32", <15 pits/150 in ² , <5 pits/30 in ²	Pass ≤ 1 spot per 30 in ²	Pass ≤ 5 spot per 30 in ²



Chemical Strip Demonstrated

Demonstrated on T-45 Pivot at JAX



Plated Pivot



Stripped Pivot



Masking Evaluation/Downselect

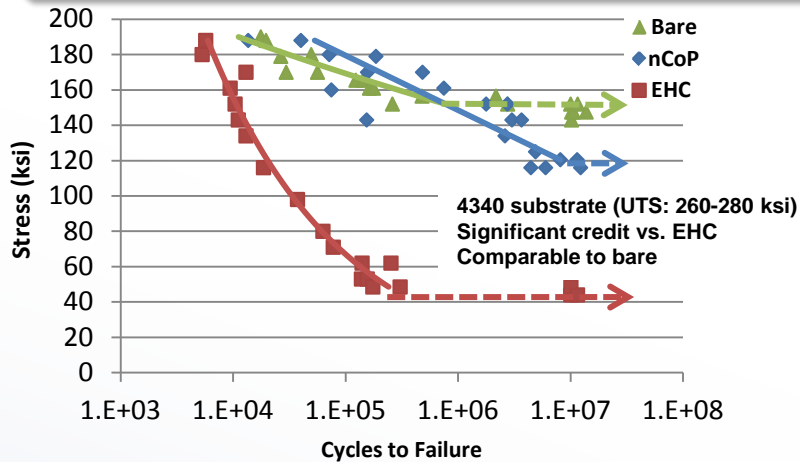


Technical Progress

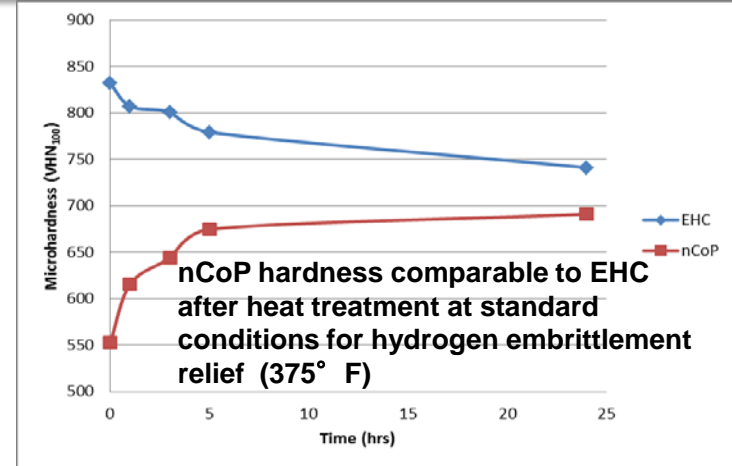
(Overview of Prior Work)



Rotating Beam Fatigue Test



nCoP Heat Treat Study



NAVAIR JAX Base line Plating - Dem/Val



EHC Plating of T-45 Pivot Assy



OSD Coupon Testing Completed



Taber Abrasion, Impact, Adhesion, Corrosion



Carburized 1018 Steel Coupons



Technical Progress

(Masking evaluation)



High Temp Wax Evaluation/Electroplaters tape

- Root cause of pitting identified from traditional electroplaters tape (breakdown of backing adhesive).
 - High Temp 3M Vinyl Tape Resolved pits

- Evaluating non-solvent based High Temp Wax (Darent Wax Company LTD)
 - Performed Thermal Analysis
 - Compatible with nCoP plating Bath
 - Initial evaluation on small mock-up samples/pieces
 - Melting Point >100 °C (212 °F)
 - Rapid Solidification
 - Ease of Use



Traditional electroplaters tape (L) and custom electrical tape (R).



Thermal Analysis of Wax



Maskant on Flat Coupons/Threaded items Evaluated at 130°C (266°F)

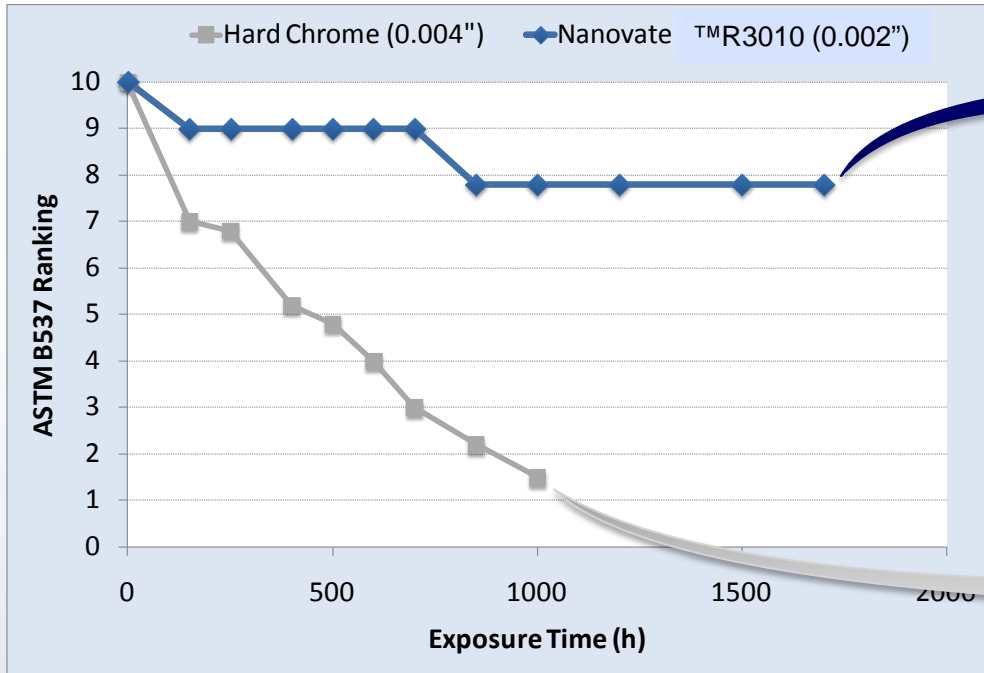


Technical Progress

(ASTM B-117 Corrosion Testing)



Salt Fog Testing (ASTM B-117)



ASTM B537 Ranking following ASTM B117 Salt Spray

Nanovate™ R3010

nCoP
192 hrs

μ-EDXRF Spectra

Coating Oxidation

Hard Chrome

EHC
192 hrs

μ-EDXRF Spectra

Substrate Corrosion



Technical Progress

(Corrosion – Beach Exposure)

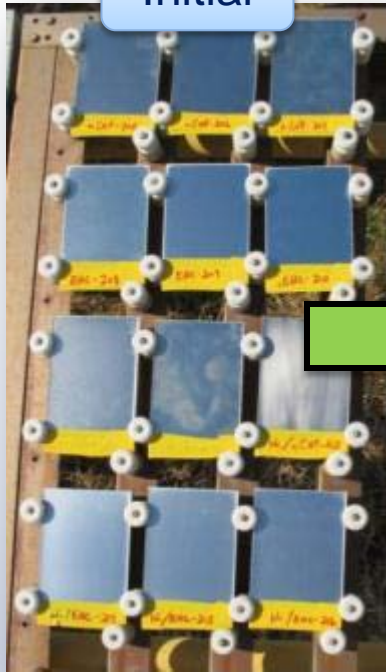


Kennedy Space Center Beach Exposure

- Beachside Atmospheric Test Facility, NASA KSC
- EHC exhibits red rust
- Discoloration consistent with cabinet testing on nCoP



Initial



EHC – 12 months



Ni+EHC – 12 months



nCoP – 12 months



Ni+nCoP – 12 months





Technical Progress

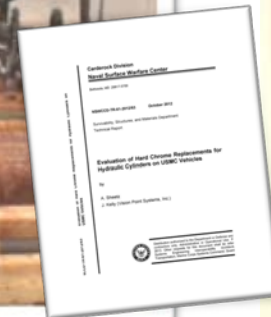
(OSD Corrosion Testing)

■ Cycling corrosion/seal wear:

Cylinder Testing Cycle (1 mil coating):

1. Cylinder cycling 1000 cycles then
2. ASTM B117 10 days

nCoP plated cylinders have completed a cumulative total of 100 days ASTM B117 and 10,000 cylinder cycles with **no reported failure due to seal leakage.**



10,000 cycles/ 100 Days
No Failures



4000 cycles/ 40 Days
EHC-2 Failed





Technical Progress

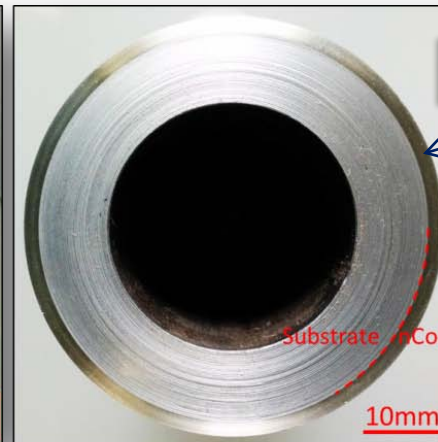
(Wear Testing for Shafting Application)

Journal Wear Testing Completed:

- nCoP demonstrated as a viable alternative for Navy propulsion shafting applications
- Wear testing showed no measurable mass loss.
- Evaluated Galvanic, general & Crevice Corrosion
- Demonstrated bond integrity on Inconel 625, 70/30 CuNi & low alloy steels
- Dem/Val on large scale shafts successfully demonstrated under an ONR Swampworks program.



Wear test equipment



Nanovate™ R3010 Plating on Navy Shaft geometries/materials



Technical Progress

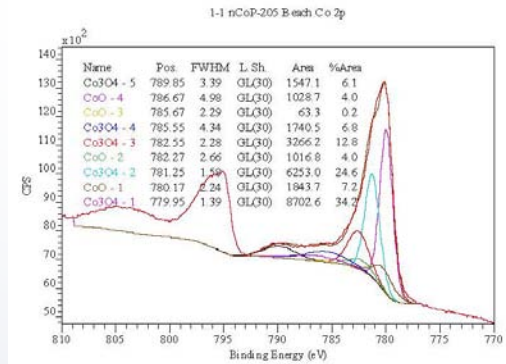
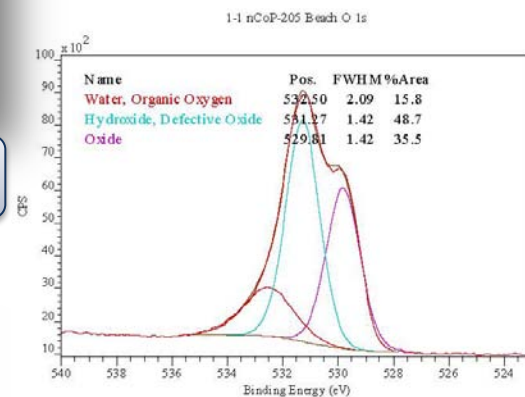
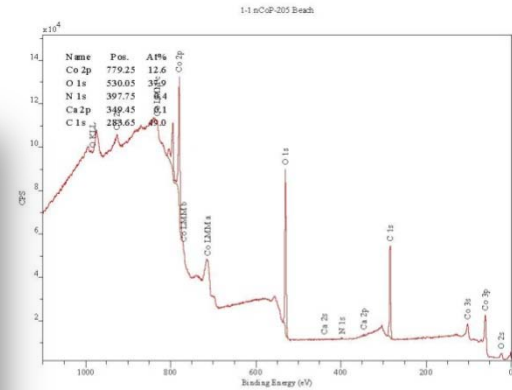
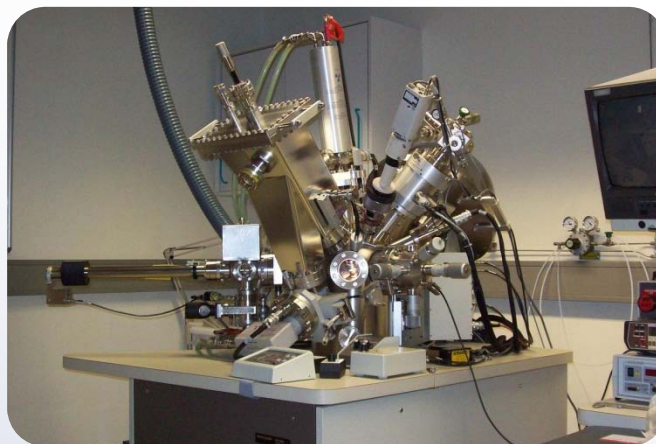
(Oxide Characterization)

Oxide Characterization Completed

- ✓ X-ray photoelectron spectroscopy (XPS) analysis determined Co oxide (Co_3O_4) and CoO on surface. **(NO IRON PRESENT)**



nCoP Coupon
(Nanovate R3010)





Technical Progress

(Endurance Rig Testing)



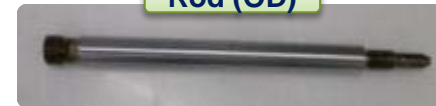
Endurance Rig Testing

- Assess wear performance vs. chrome as an ID actuator
- Test developed by Messier-Dowty
 - 20,000 Cycles
 - Criteria -- Less than one drop of hydraulic fluid in 25 cycles and acceptable wear
 - Observe effect of surface finish, seal types, and hardening condition



nCoP tested as good or better than EHC

Rod (OD)



Cylinder (ID)

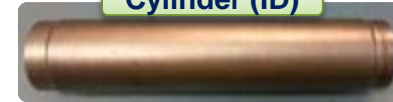
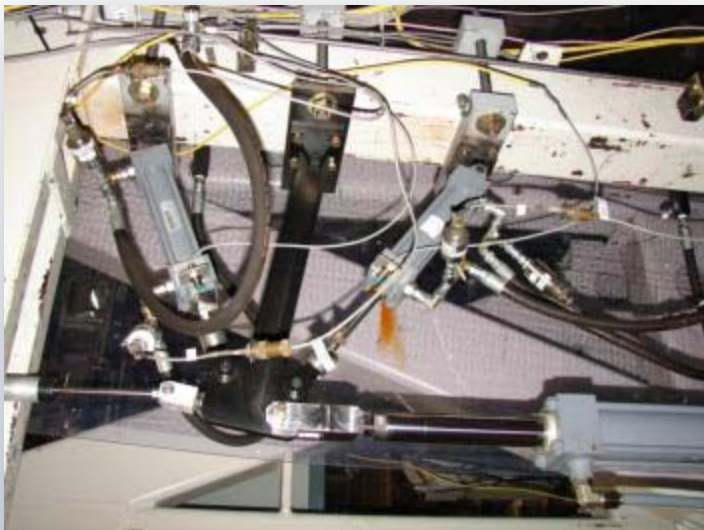
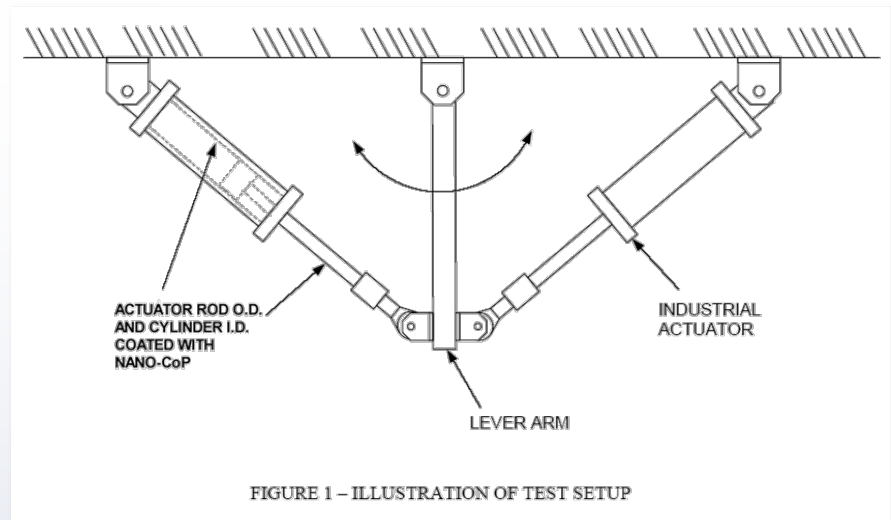


Image of Endurance Rig Test



Endurance Rig Test Schematic





Technical Progress

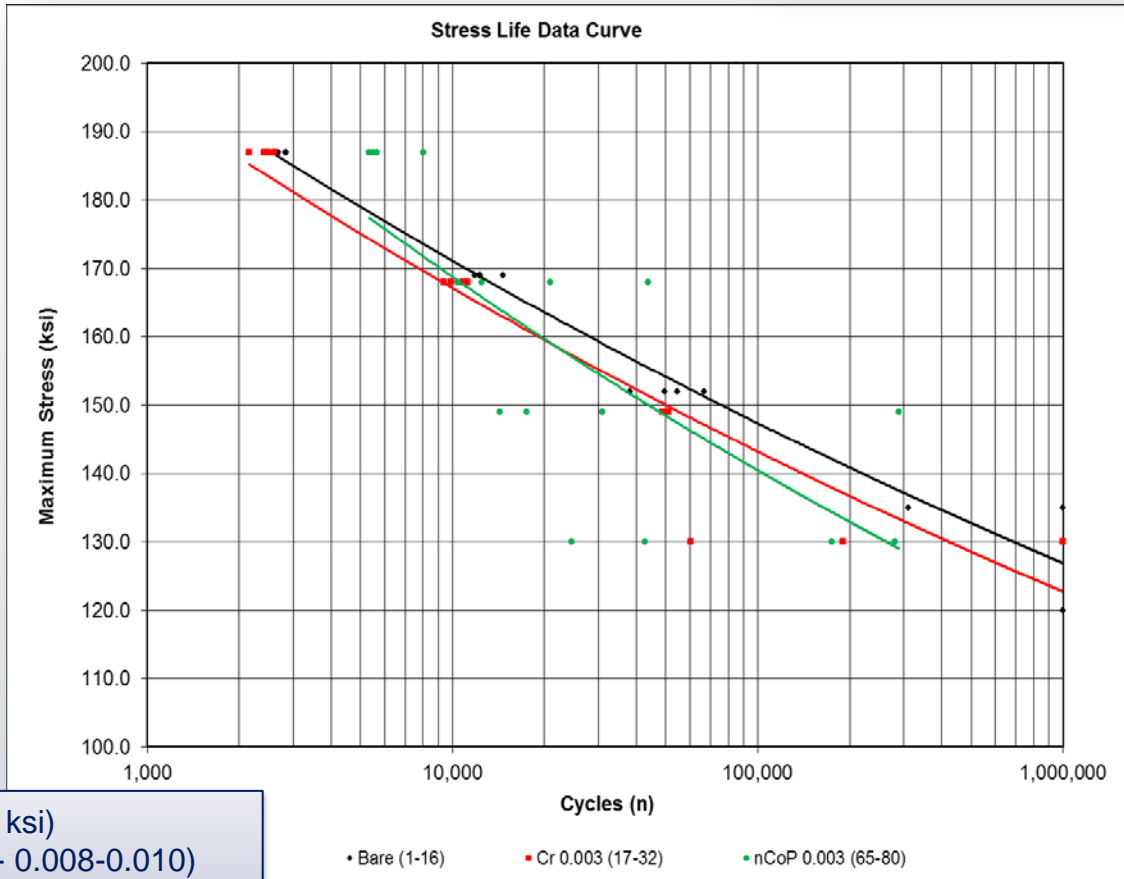
(Fatigue Testing)



Axial Fatigue Testing



0.003" Coating thickness



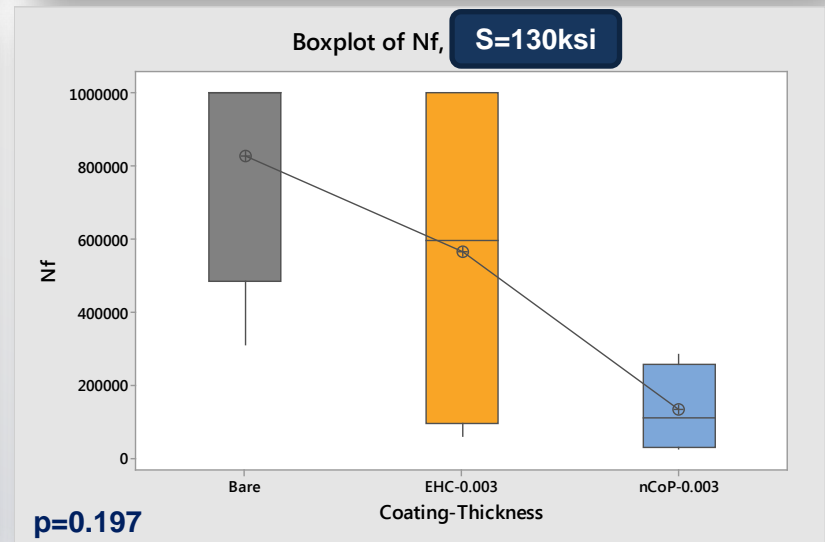
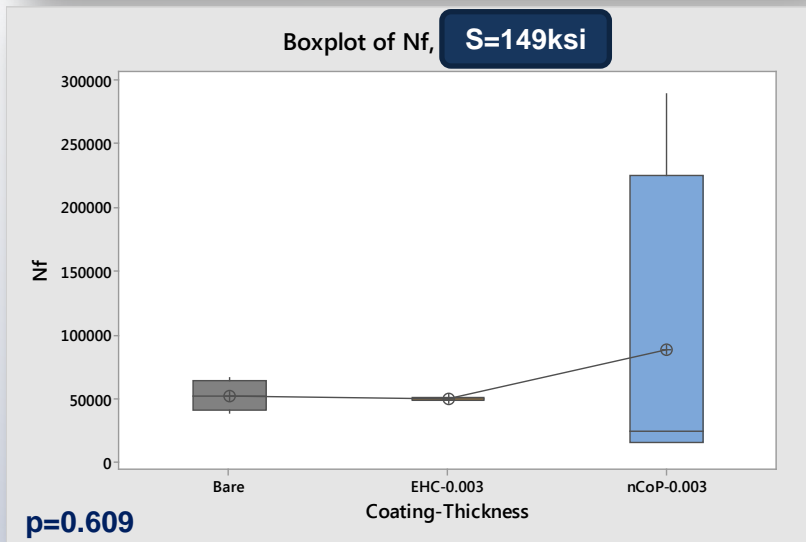
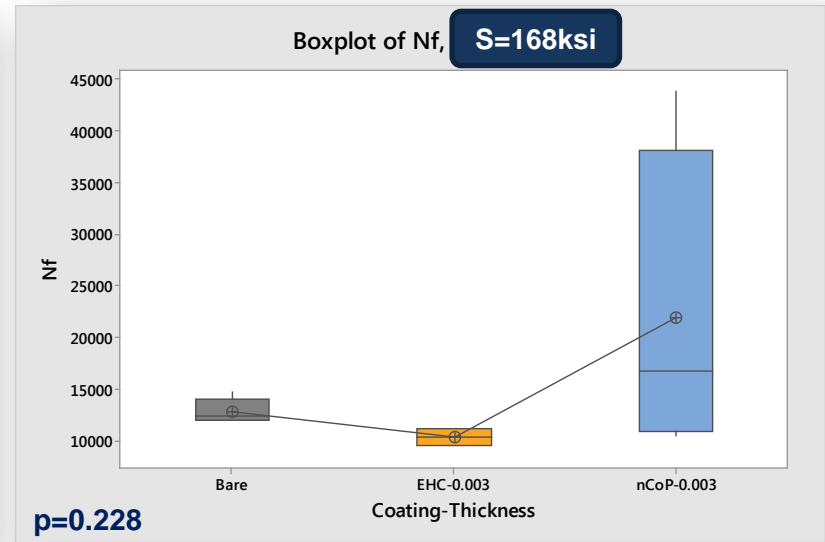
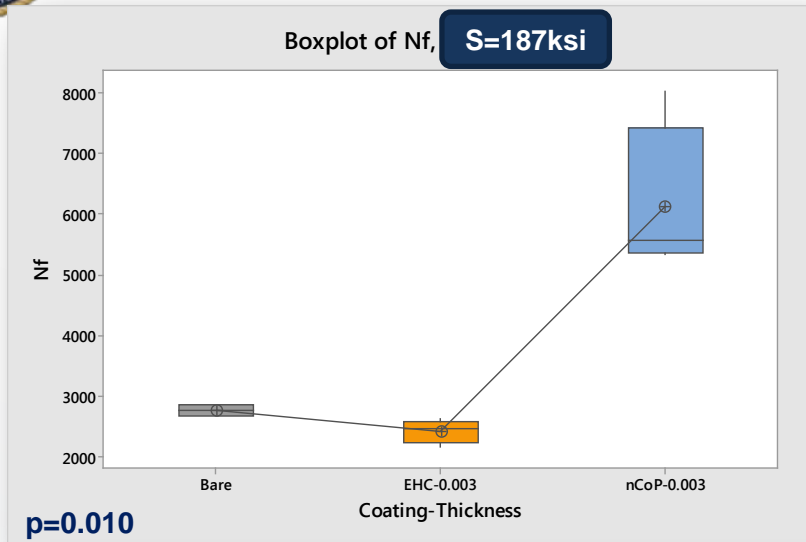
Test Conditions

- 4340 steel (260-280 ksi)
- Shot peened (S110 - 0.008-0.010)
- 16 Ra Minimum
- R ratio: R = -1, Freq: 20 Hz
- Loads: 85% YS to 10⁶ Cycles



Technical Progress

(Fatigue Testing)



Boxplot comparing bare with EHC and nCoP coated samples at a thickness of 0.003” at each load level.



Technical Progress

(Component Dem/Val Electroplating Process)



NAVAIR JAX Plating Dem/Val - May 2011

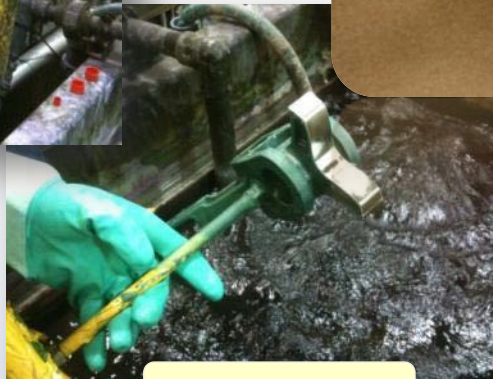
■ nCoP Plating of T-45 Arresting Hook Pivot



Mask/Rack



nCoP Plate



As Plated



Ready for Field Demo





Field Demonstrations

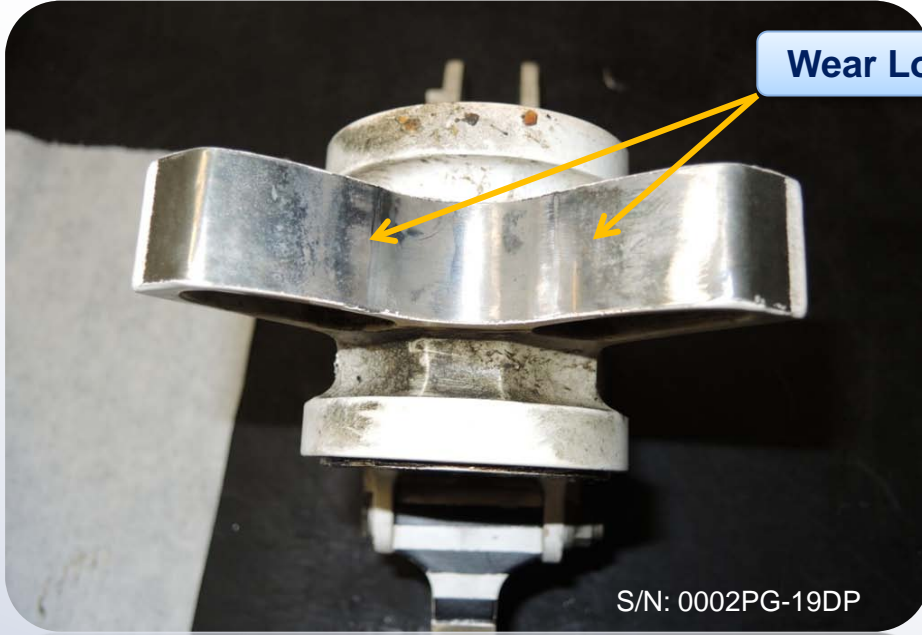
(T-45 Pivot Assy)



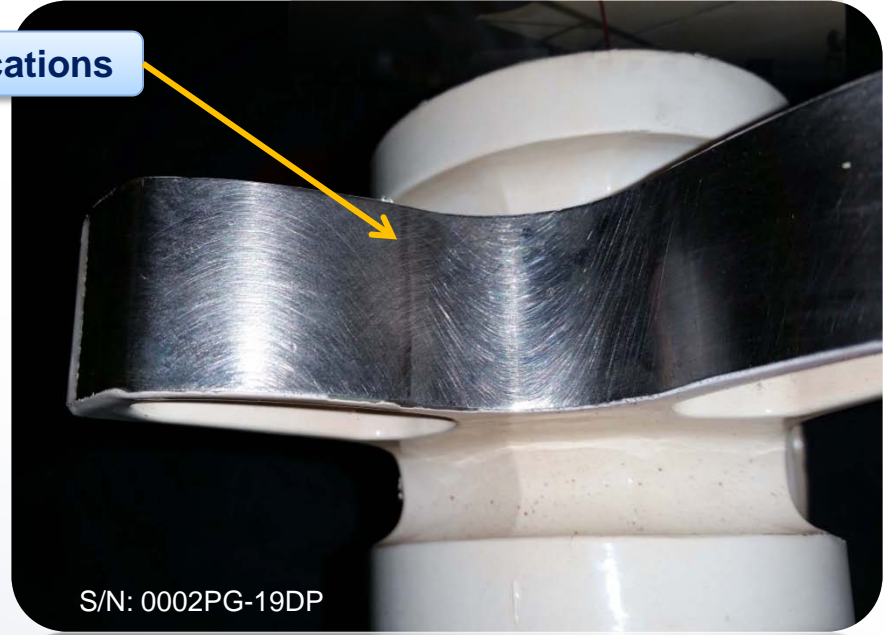
Dem/Val Component Field Inspection

Field Performance: T-45 Arresting Hook Pivot

- nCoP plated pivot inspected after 72 & 97 arrestments
- Passed inspection & reinstalled on A/C
- 116 arrestments w/ 900 ± 15 Total Flight Hrs as of Nov 2014



nCoP – After 72 arrestments, 705 ± 10 Flight Hrs



nCoP – After 97 arrestments, 825 ± 15 Flight Hrs



Field Demonstrations

(T-45 Pivot Assy)

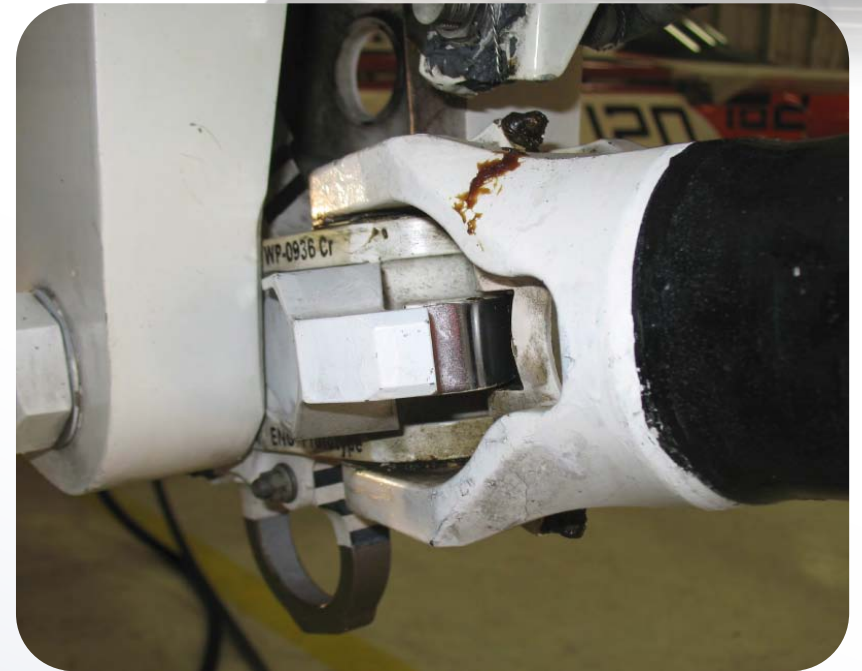


Dem/Val Component Field Inspection

- **Field Performance: T-45 Arresting Hook Pivot**
 - nCoP Plated Pivot reaches 116 Arrestments!
 - Baseline still at 63 Arrestments



nCoP – After 116 arrestments
(BUNO: 165629)



EHC – After 63 arrestments
(BUNO: 165463)



Field Demonstrations

(M9 ACE Cylinder)



M9 ACE Cylinder Dem/Val

- Assembled/Pressure Tested at Marine Corp Depot, Albany, GA
- Installed on Vehicle – Mar 2014
- Field tested at Panama City



Nanovate™ R3010 plated cylinder installed on M9 ACE for field demonstration



Nanovate™ R3010 plated Hydraulic Cylinder for M9 ACE (Armored Combat Earthmover)



Marine Corps MK48 Logistics Vehicle System, M9 ACE



Field Demonstrations

(Lifting Arm Pin)

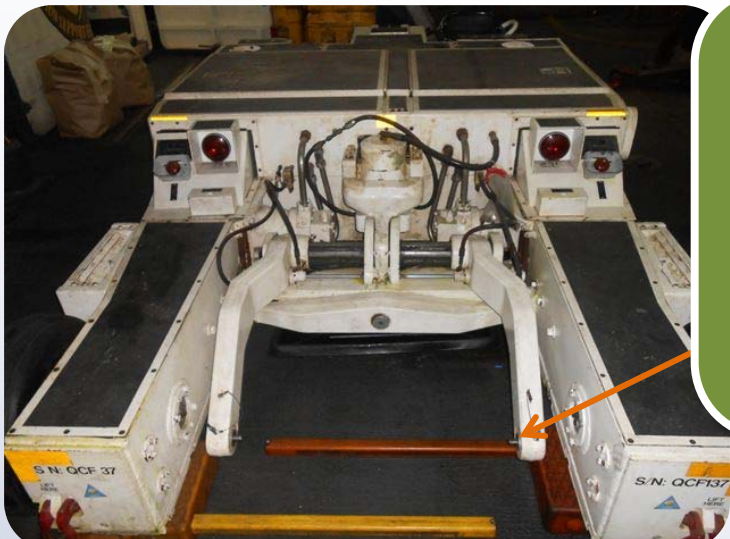


Dem/Val Component on Carrier (CVN-75)

- Pins installed Jul 2013; Onboard CVN-75 USS Harry S Truman
- >672 A/C moves since installation
- Pins passed 91 day PMS NDI Inspections
- Fleet saving ~2.5 man hrs/pin to clean/prep for NDI
- nCoP coated pins outperformed baseline
- Endorsement Letter provided by cognizant Engineer



Dem/Val Pin prior to NDI



Spotting Dolly (A/S32A-32, S/N: QCF137) with Dem/Val pins on carrier

"These pins are a dream to work with; considering no prep work is required for NDI. Hopefully this project leads to all pins, including the adapter pins having this coating."

-- Senior Chief on board the CVN 75

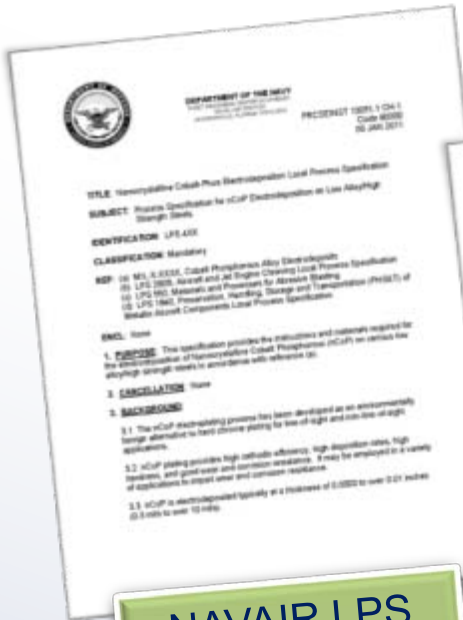


Lifting Arm Pin in place



Technology Transfer

(Specification Development)



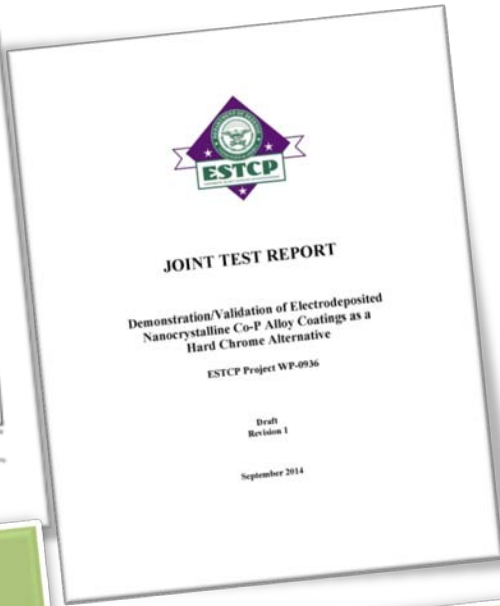
**NAVAIR LPS
(Draft Version)**



**MIL Spec
(MIL-DTL-32502)**



**AMS Spec
(B13AA)**



**JTR Draft
(Joint Test Report)**



Percent Complete



Questions

Ruben Prado, CEF



Principal Investigator
Naval Air Systems Command
904-790-6381
Ruben.prado@navy.mil

Jack Benfer, M.S.



Co-Principal Investigator
Naval Air Systems Command
904-790-6405
John.benfer@navy.mil

Neil Mahalanobis



Unit Manager
Integran Technologies, Inc.
416-675-6266 x 375
mahalanobis@integran.com





Backup Material



Acronyms and Symbols

CDR – Critical Design Review
DOE – Design of Experiment
EDS – Energy Dispersive Spectroscopy
EHC – electrolytic hard chrome
FOC – Full Operating Capability
FRCSE – Fleet Readiness Center South East
HE – Hydrogen Embrittlement
ID – Internal Diameter
ISSC – In Service Support Center
JTP – Joint Test Protocol
LED – Local Engineering Instruction
LOS – Line of Sight
LPS – Local Process Specification
MIPR - Military Interdepartmental Purchase Request
NAVAIR – Naval Air Systems Command
NDI - Non Destructive Inspection
NLOS – Non-line-of-sight
nCoP – nanocrystalline cobalt-phosphorus
OD – Outer Diameter
OSD – Office of the Secretary of Defence
PEO – Program Executive Office
PMA – Program Manager - Air
SEM – Scanning Electron Microscope
SRR – System Requirements Review
 μ -EDXRF – Micro energy dispersive X-ray fluorescence



Publications

Papers/Publications Since IPR 2010

D. Facchini, J. McCrea, P. Lin, F. Gonzalez and G. Palumbo, "Microstructural Engineering of Surfaces: Applications for Nanocrystalline and Grain Boundary Engineered Materials in Aerospace and Defense", proceedings of the SURFAIR Conference, Biarritz FR, June 10th, 2010

Prado, R.A., Benfer, J., and Facchini, D., 2011. Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative. In: ASETS Defense, Sustainable Surface Engineering for Aerospace & Defense, New Orleans LA, February 8-11, 2011.

F. Gonzalez, "Electroplate Alternatives to Hard Chrome: Nanocrystalline Metals and Alloys", proceedings of NASF SUR/FIN 2010, Grand Rapids, MI, June 16th, 2010

Prado, R.A., Benfer, J., Facchini, D., Mahalanobis, N., Gonzalez, F. and Tomantschger, K., 2011. Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative for use in DoD Acquisition Programs. To be presented at: NASF SUR/FIN 2011, Chicago II, June 13-15, 2011.

Patents/Patent Applications

U.S.7,910,224 (2011), US 7,824,774 (2010), US 7,320,832 (2008): Fine-grained metallic coatings having the coefficient of thermal expansion matched to the one of the substrate

US 5,433,797 (1995): Nanocrystalline metals

US 5,352,266 (1994): Nanocrystalline metals and process of producing the same

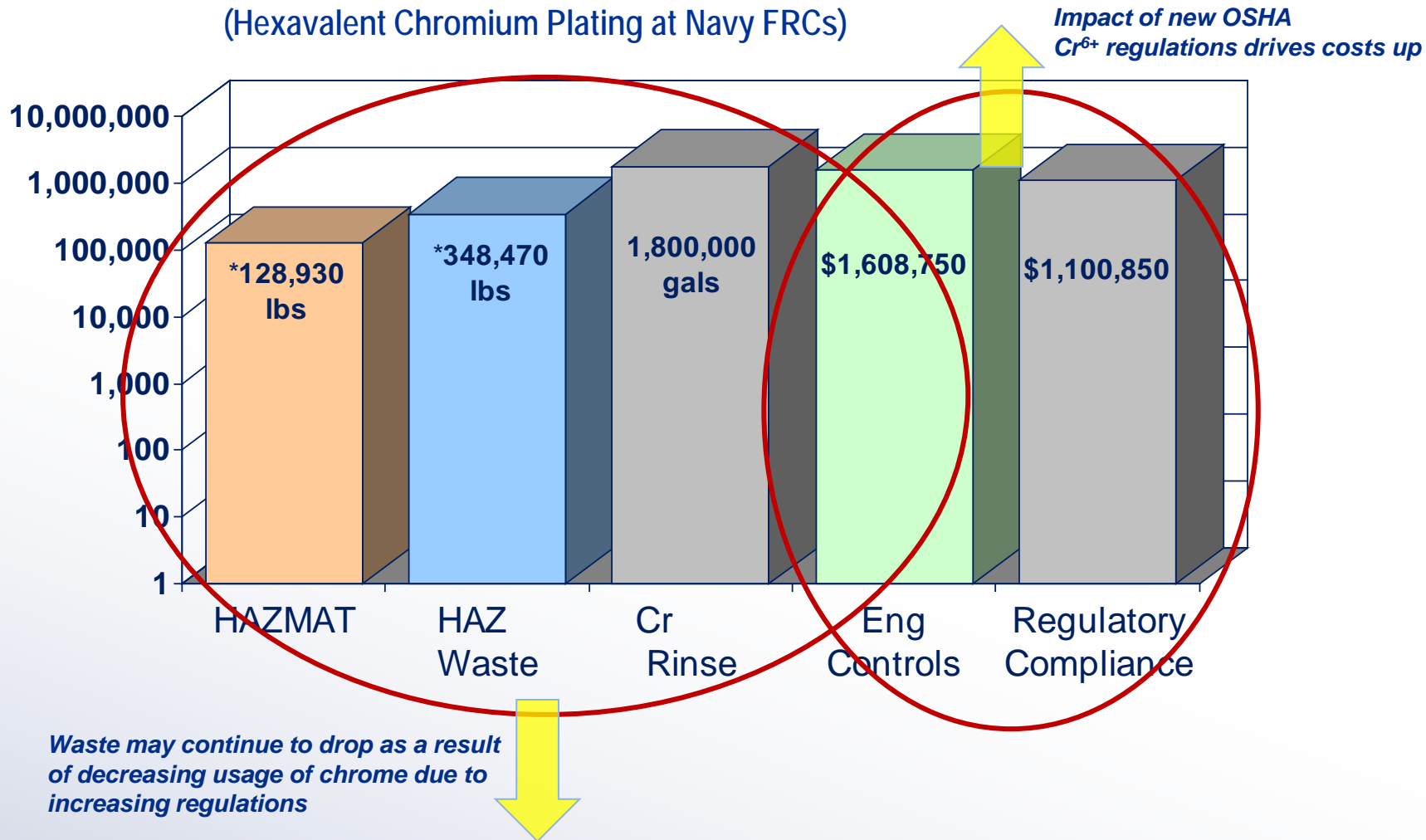
US 2010/0304182 (2010): Electrodeposited metallic-materials comprising cobalt



Environmental – Cost Benefits

■ Estimated NAVAIR P2 Savings over 10 Yrs

(Hexavalent Chromium Plating at Navy FRCs)



Note: the above projected savings are assumptions based on FRC-SE data extrapolated to other Navy FRCs. Estimated amounts due to chrome plating based on average Environmental Systems Allocation (ESA) data extrapolated across all FRCs over a 10 yr period



Coating Properties

(Nanovate™ R3010 vs. EHC)

Property	Test Method	Applicable Standard	Nanovate™R3010	EHC
Appearance and porosity	Visual and microscopic inspection	N/A	Free from pits, microcracks and pores	Microcracked
Grain Size	X-Ray Diffractometry	N/A	8-15 nm	-
Hardness	Vickers Microhardness	ASTM B578	550-600 VHN (as-deposited)	Min. 600 VHN
			600-750 VHN (heat treated)	-
Ductility	Bend Test	ASTM B489	2-7%	<1%
Adhesive Wear	Pin on Disc (Al ₂ O ₃ Ball)	ASTM G99	6-7 x 10 ⁻⁶ mm ³ /Nm	9-11 x 10 ⁻⁶ mm ³ /Nm
Coefficient of friction			0.4-0.5	0.7
Pin Wear			Mild	Severe



Coating Properties

(Nanovate™ R3010 vs. EHC)

Property	Test Method	Applicable Standard	Nanovate™ R3010	EHC
Abrasive Wear	Taber Wear (CS-17 wheels)	ASTM D4060	17 mg/1000 cycles	4 mg/1000 cycles
Corrosion	Salt Spray	ASTM B117	0.003" thick Pass 165 hrs 0.002" thick Protection Rating 7 (ASTM B537) @ 1000 hours	0.003" thick Fail 165 hrs 0.004" thick Protection Rating 2 (ASTM B537) @ 1000 hours
Deposit Stress	Internal Stress Test	N/A	10-15 ksi (Tensile)	Cracked – Exceeds cohesive strength
Fatigue	Rotating Beam Fatigue	N/A	Comparable to bare at high loads. Small debit compared to bare at low loads. Credit compared to EHC.	Significant debit compared to bare at all loads.