



Nanocrystalline Cobalt-Phosphorus Electroplating as an Alternative to Hard Chromium Electroplating



(Project # WP-0936)

Ruben A. Prado, CEF
(Principal Investigator)

Inorganic Coatings SME
NAVAIR Associate Fellow

John E. Benfer, M.S.
(Co-Principal Investigator)

Corrosion Engineering Team Lead
NAVAIR Associate Fellow

ASETS Defense Workshop
Sustainable Surface Engineering for Aerospace & Defense
(August 2012)

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE AUG 2012		2. REPORT TYPE		3. DATES COVERED 00-00-2012 to 00-00-2012	
4. TITLE AND SUBTITLE Nanocrystalline Cobalt-Phosphorous Electroplating as an Alternative to Hard Chromium Electroplating				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,47123 Buse Road,Patuxent River,MD,20670				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 2012: Sustainable Surface Engineering for Aerospace and Defense Workshop, August 27-30, 2012, San Diego, CA. Sponsored by SERDP/ESTCP.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 36	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:



- Diana Facchini, Neil Mahalanobis
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 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
- ❑ Initiate DoD and OEM approval process



Demo Site: FRC JAX



Technical Approach

(Dem/Val 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

Technical Approach

(Technology Description)

■ Coating applied by electrodeposition

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



■ Electrodeposited nanocrystalline materials

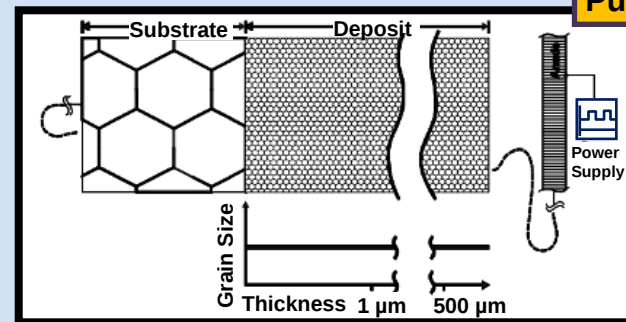
- *Favors nucleation of new grains over growth
- Results in an ultra-fine grain structure
- Uniform throughout thickness

■ Leads to unique properties

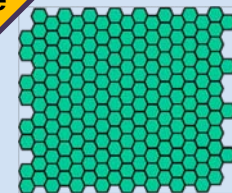
- ↑ Yield Strength, wear, ultimate tensile strength
- ↑ Density
- ↓ Coefficient of friction

**Smaller grain size impedes dislocation movement and increases yield strength*

Nanocrystalline Electrodeposit



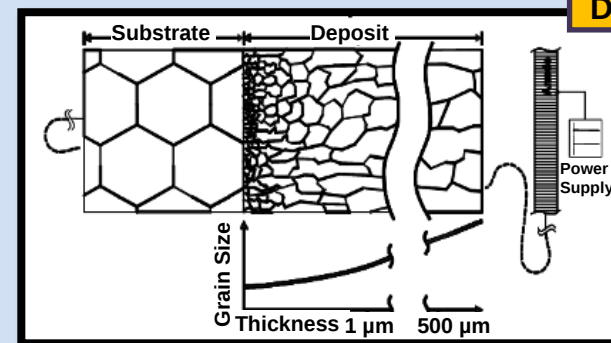
Pulse



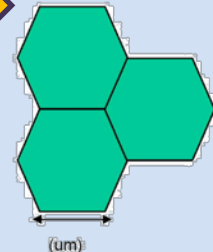
*Nanocrystalline
($< 100 \text{ nm}$)

**nCoP electrodeposits have grains of $\leq 20 \text{ nm}$*

Conventional Electrodeposit



DC



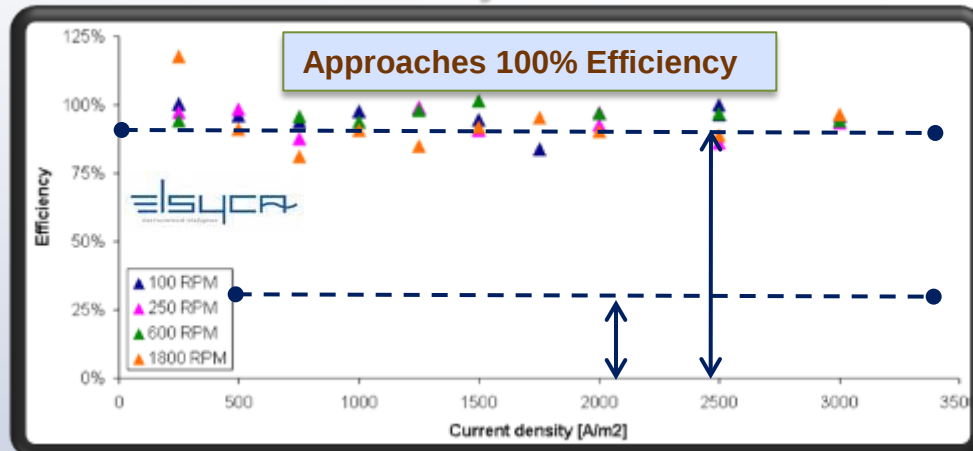
Polycrystalline
($10-100 \mu\text{m}$)

■ Process Comparison

	Nanovate™ CoP	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

*Co PEL is 20 µg/m3

■ Cathode Efficiency



Nanovate™ CoP Plating Tank at FRCSE
Temp = 185°F

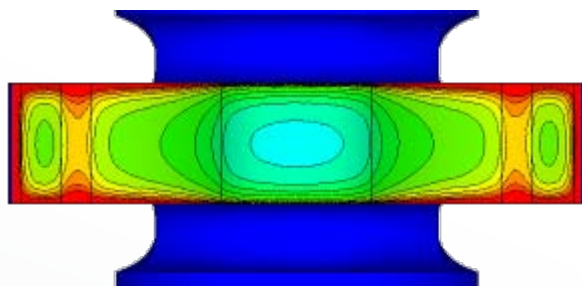
- ≈5X faster than Chrome plating
- Increased throughput
- One nCo-P tank can replace several hard chrome tanks
- Bath is Stable



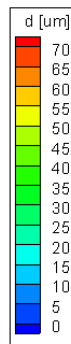
Overview of Prior Work



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

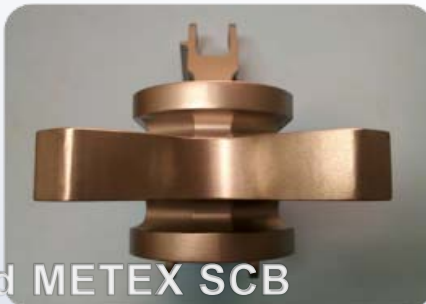


Chemical Strip Demonstrated

Demonstrated on T-45 Pivot at JAX



Plated Pivot



Stripped Pivot



Masking Evaluation/Downselect

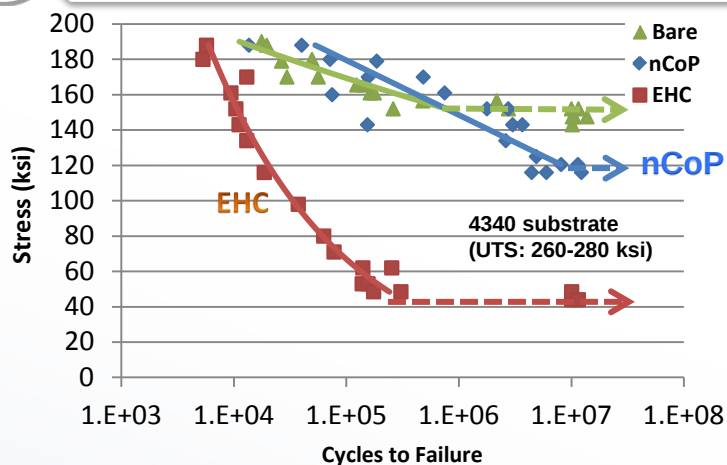




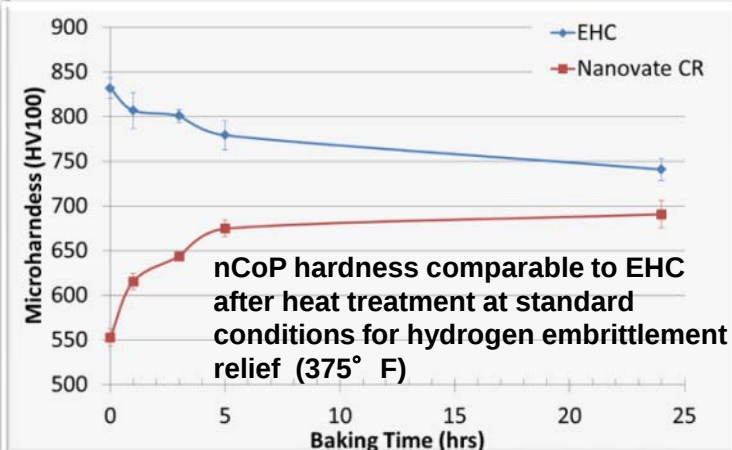
Overview of Prior Work



Rotating Beam Fatigue Test



nCoP Heat Treat Study



OSD Coupon Testing Completed



Taber Abrasion, Impact, Adhesion, Corrosion



Carburized 1018 Steel Coupons

LED TO RIG TESTING



NAVAIR JAX Base line Plating - Dem/Val



EHC Plating of T-45 Pivot Assy

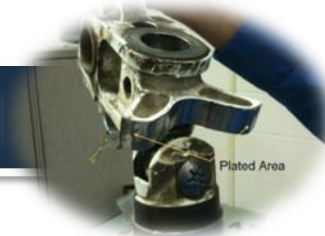


Technical Progress

(Component Dem/Val Plating)



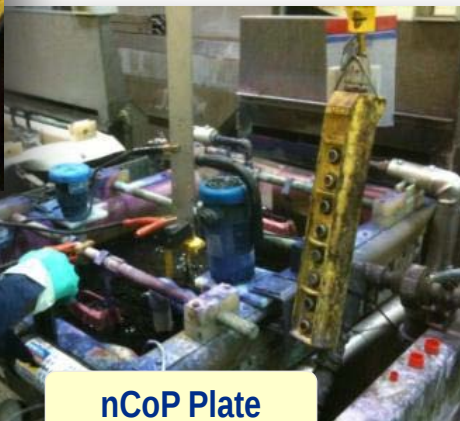
NAVAIR JAX Plating Dem/Val - May 2011



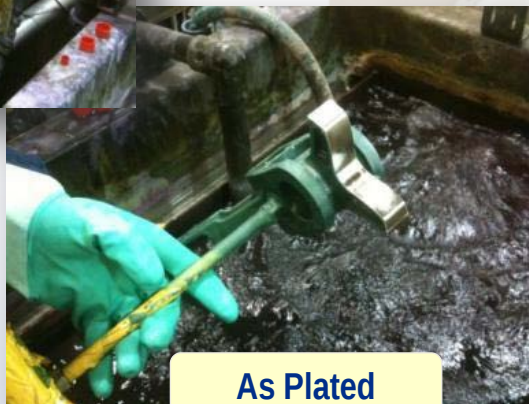
■ nCoP Plating of T-45 Arresting Hook Pivot



Mask/Rack



nCoP Plate



As Plated



Ready for Field Demo





Technical Progress

(Field Demonstration)



Dem/Val Component on Aircraft!

- T-45 Arresting Hook Pivot Assembly
- Installed Mar 2012 (BUNO# 165479) ≈ 30 Traps



Dem/Val Component installed on T-45 Goshawk Trainer Aircraft NAS Meridian, MS



nCoP Plated Dem/Val Component



Technical Progress

(NESDI & OSD Leveraged Effort – Phase II)



■ Phase II OSD Rig Testing:

Cylinder Testing Cycle (1 mil coating):

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

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



nCoP



10,000 cycles/ 100 Days
No Failures

EHC



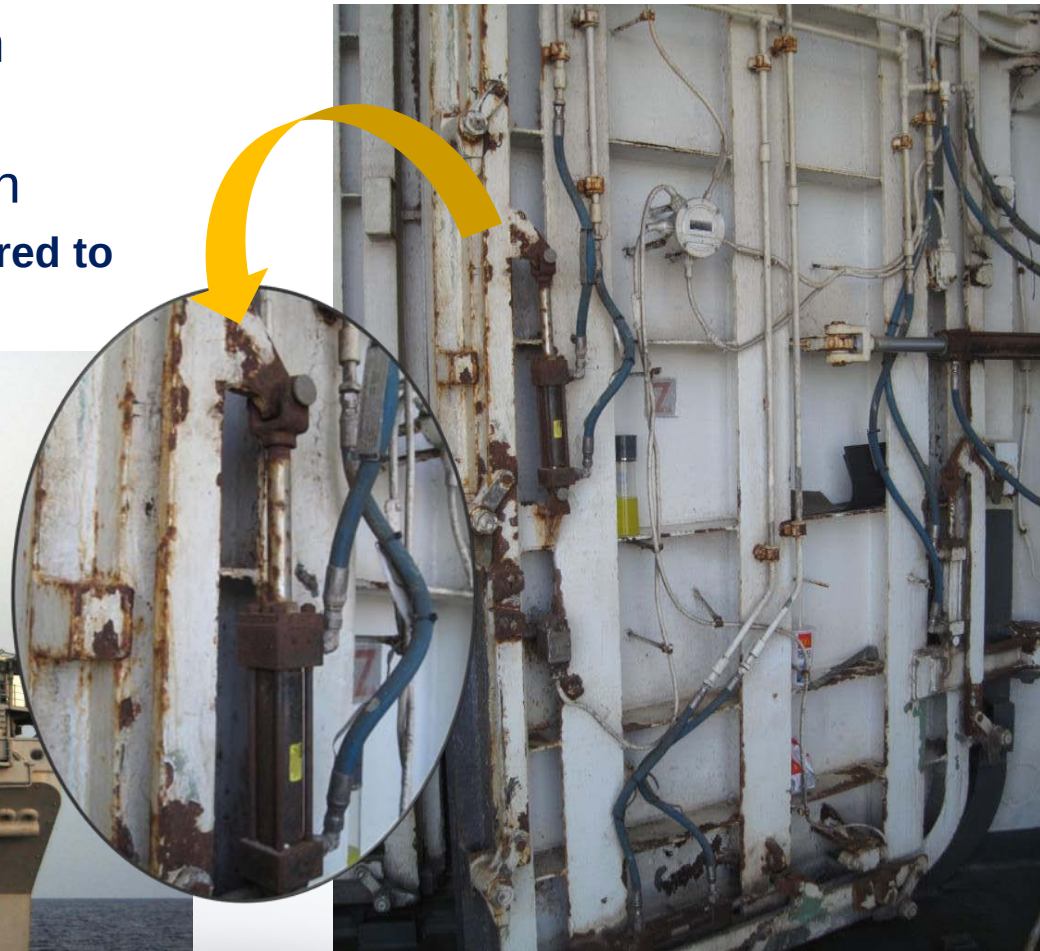
4000 cycles/ 40 Days
EHC-1 Still in test
EHC-2 Failed

LHD1 Stern Gate

- Replace Cr plated shaft with nCoP
- Perform Field Demonstration
- Evaluate Performance as compared to baseline



U.S. Navy multipurpose amphibious assault ship



Stern Gate Piston Shaft



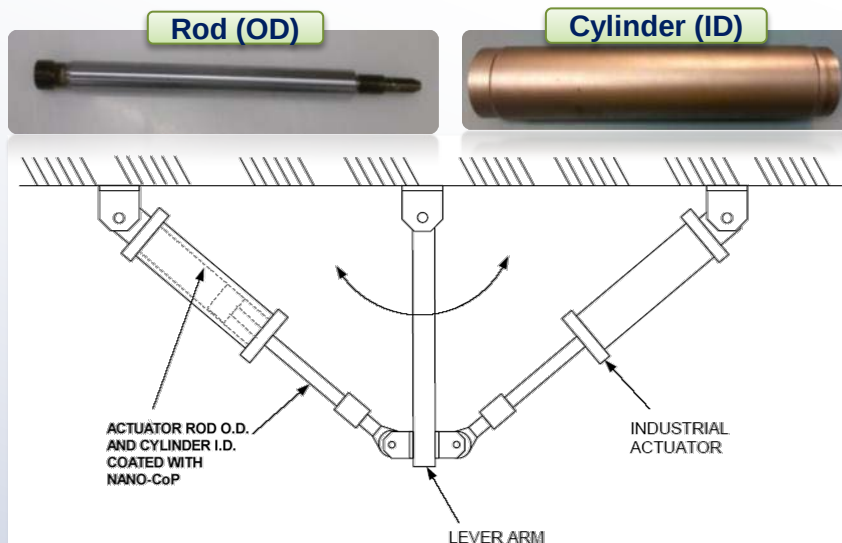
Technical Progress

(Endurance Rig Testing)



Plating/Grinding Completed for Messier Testing

- Assess wear performance vs. chrome as an ID actuator
- Currently conducting dimensional inspections
- ECD is Q4/2012
- Test developed by Messier-Dowty
 - 20,000 Cycles
 - Observe effect of surface finish, seal types, and hardening condition



Endurance Rig Test Schematic

Coating	Surface Finish (Microinches)	Piston Seal	Rod Seal
EHC	4-6, 12-16	Buna-N Tee Seal Nitrile Butadiene Rubber	Buna-N Tee Seal Nitrile Butadiene Rubber
nCoP	4-6, 12-16		
nCoP HE Bake	4-6, 12-16		
nCoP Max Heat Treat	4-6, 12-16		
EHC	12-16	Viton Tee Seal Synthetic Rubber Fluoropolymer Elastomer	Viton Tee Seal Synthetic Rubber Fluoropolymer Elastomer
nCoP	12-16		
EHC	12-16	PTFE Cap	Spring Energized PTFE
nCoP	12-16		
EHC	12-16	Buna-N O-Ring/Back-up - Nitrile Butadiene Rubber O-Ring	Buna-N O-Ring/Back-up - Nitrile Butadiene Rubber O-Ring
nCoP	12-16		

***\$121K In kind funding (Messier-Dowty)**



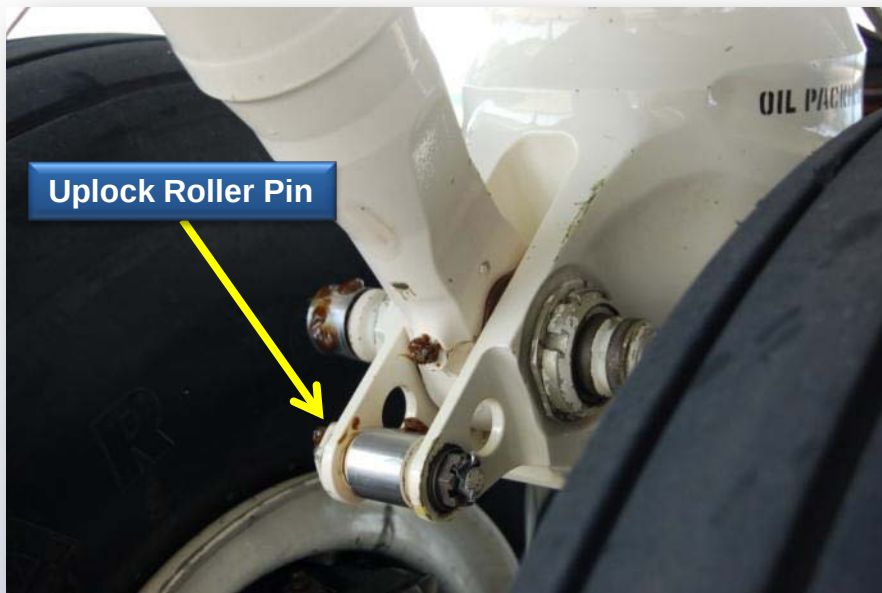
Technical Progress

(P-3 Producibility Item)



P-3 Uplock Roller Pin

- P-3 Producibility Item at JAX
- Field evaluation Planned
- Interested Air Programs?



Existing chrome Plated Roller Pin
Shown on P-3 MLG

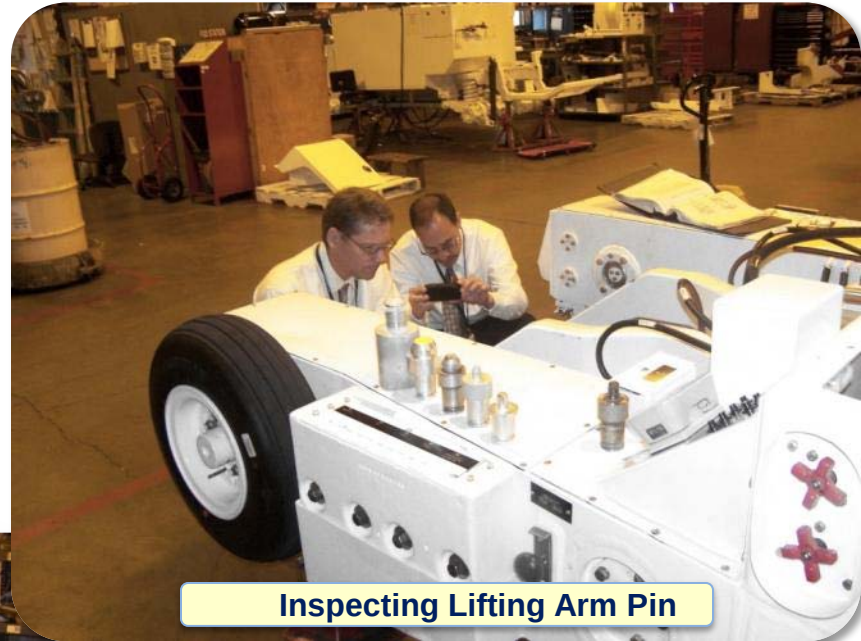


nCoP Plated Uplock Roller Pins

Technical Progress

(Spotting Dolly Lifting Pin)

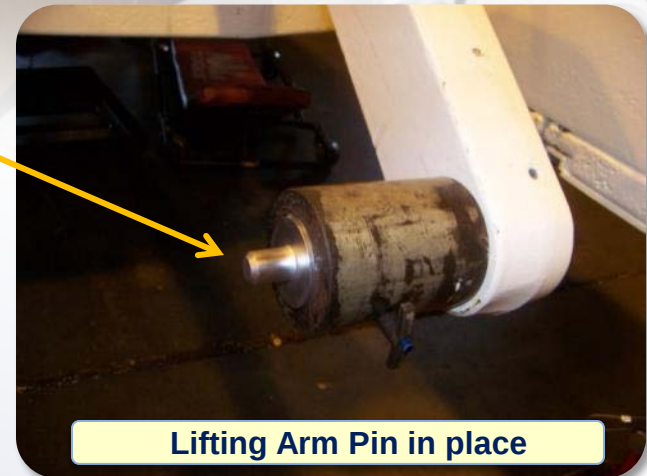
- Visit to Solomons to assess Spotting Dolly Lifting Arm Pin
- Obtain Lifting Pins for Plating
- Fit/Function Confirmed
- Scheduled for Plating



Inspecting Lifting Arm Pin



Spotting Dolly undergoing Maintenance



Lifting Arm Pin in place



Technical Progress

(Joint Test Protocol - Demonstration/ Validation)



24 Core Tests Defined in JTP

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

- JTP Testing in Progress
- T-45 Dem/Val component on Aircraft
- 50% of Core Tests Completed
- ✓ = Completed Tests, T = In Test, P = Plating

Approved – Feb 2011



DEMONSTRATION PLAN

Demonstration/Validation of Electrodeposited
Nanocrystalline Co-P Alloy Coatings as a
Hard Chrome Alternative

ESTCP Project WP-0036

Robert Probst and John Butler
Naval Air Systems Command

Steve Farnham and Neil Mahalingam
Integrated Technologies, Inc.

Northrop

Approved – Feb 2011



JOINT TEST PROTOCOL

Demonstration/Validation of Electrodeposited
Nanocrystalline Co-P Alloy Coatings as a
Hard Chrome Alternative

ESTCP Project WP-0036



Revision 3 - February 2011
FINAL



Technical Progress

(Fluid Compatibility)



Assess nCoP ability to withstand operational service conditions and overhaul fluids

Fluid	Purpose	nCoP	EHC
MIL-PRF-83282	Hydraulic	PASS	-
MIL-PRF-680	degreaser	PASS	-
Fluorescent penetrant	NDI	PASS	-
Nital	Grind burn	FAIL	*PASS
Ammonium persulfate	Grind burn etch	FAIL	*PASS
Cimstar 40	Grinding fluid	PASS	-
Turco 4181L Alkaline Cleaner	Cleaner	PASS	-
MIL PRF 85570 type 2	Cleaner	PASS	-
Bioact 280	Cleaner	PASS	-
Chlorine Bleach	Disinfectant	FAIL	*PASS

**EHC samples showed some form of minor attack. However, it did pass according to JTP acceptance criteria.*



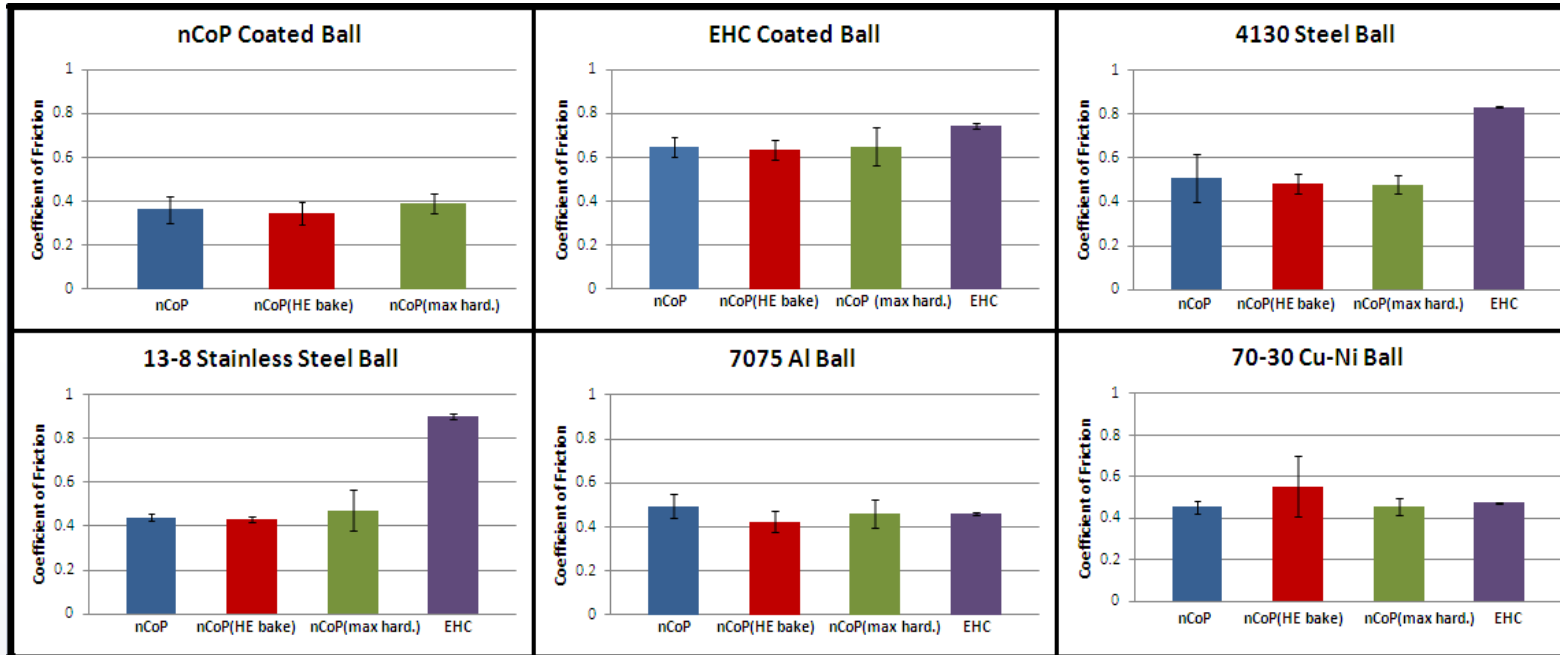
Technical Progress

Sliding Wear



- Pin-on-Disc testing conducted as per ASTM G99
("Standard Test Method for Wear Testing on a Pin on Disc Apparatus")

Coefficient of Friction Acceptance Criteria:
 $nCoP \leq EHC$



Coating	Pin Material				
	EHC coated	4130	13-8 stainless	7075 Al	70-30 Cu-Ni
nCoP	✓PASS	✓PASS	✓PASS	✓PASS	✓PASS
nCoP (HE bake)	✓PASS	✓PASS	✓PASS	✓PASS	✓PASS
nCoP (Max hardness)	✓PASS	✓PASS	✓PASS	✓PASS	✓PASS



* Does not include nCoP ball on EHC results

Technical Progress

(Abrasive Wear)

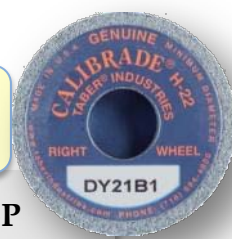
- Taber wear testing to assess abrasive wear resistance of coatings
- Performed ASTM D4060
- Performed ASTM F1978



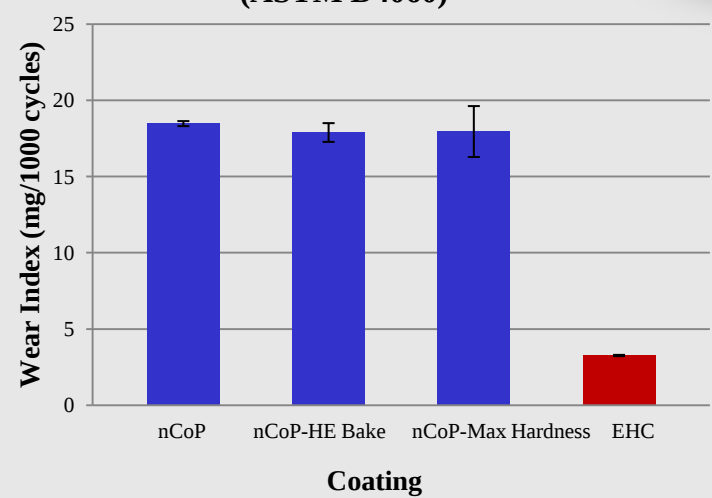
- CS-17 wheels
- 1000g load



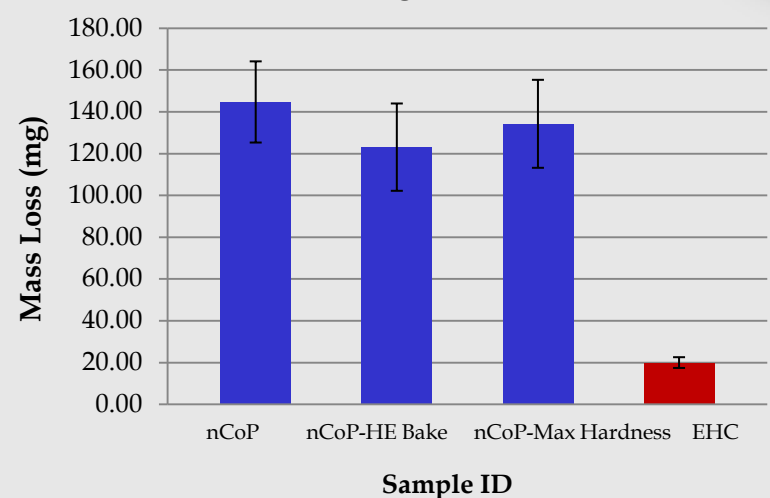
- H-22 wheels
- 250g load



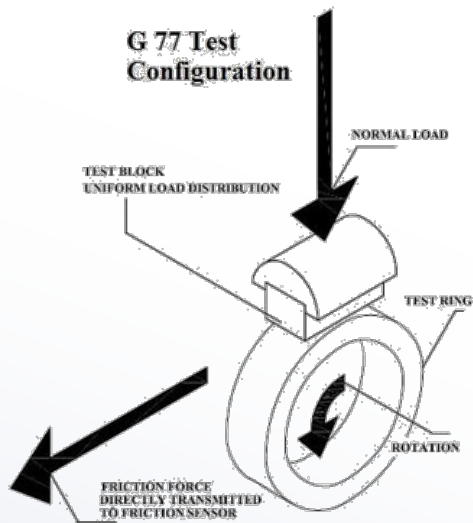
Wear Index of nCoP and EHC Coatings (ASTM D4060)



Total Mass Loss over 2000 cycles of nCoP and EHC Coatings (ASTM F1978)

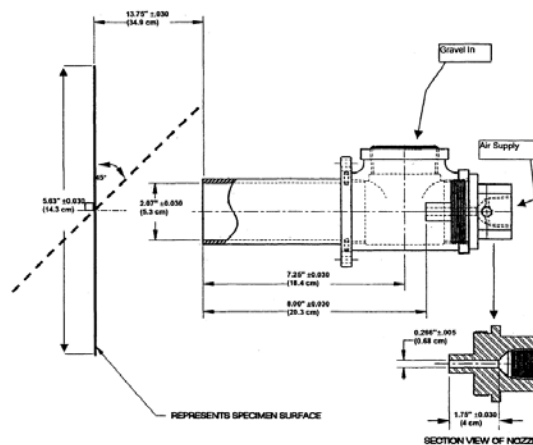


Wear Samples plated and at Boeing for Testing



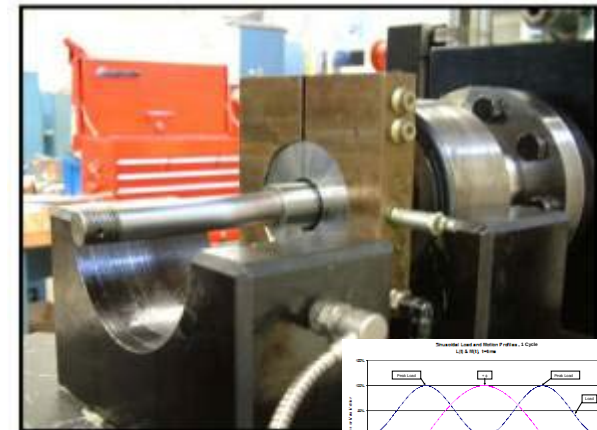
FALEX Block on Ring

- Test per ASTM G77
- determines the resistance of materials to sliding wear
- Different Alloy/Coatings against Ring



Gravelometry

- Test per ASTM D3170
- Specimens mounted perpendicular to projected path
- Pea size gravel; air pressure 70 psi



SATEC Oscillating Load

- Boeing Specific Test
- Pin/Bushing Oscillating Wear Test
- Constant/ Sinusoidal load-motion profile





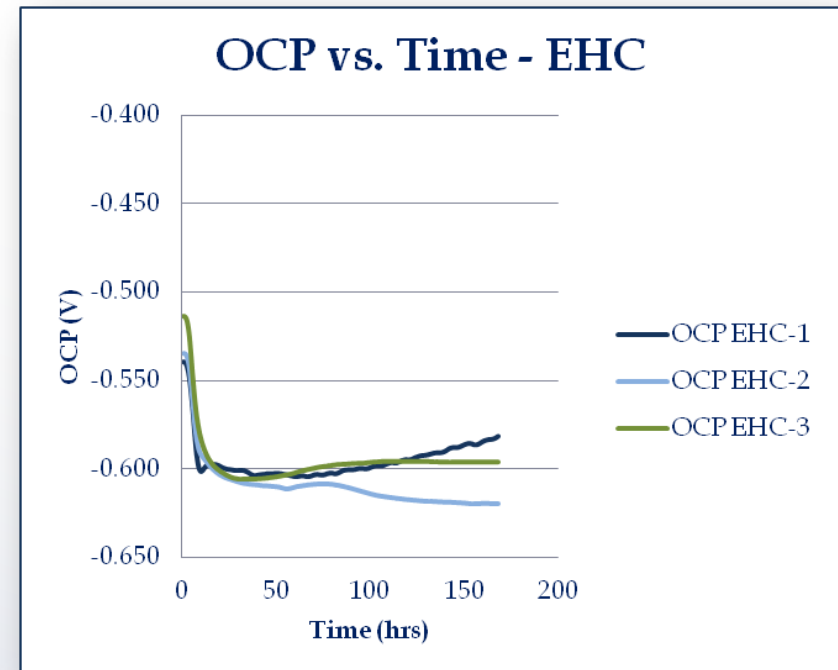
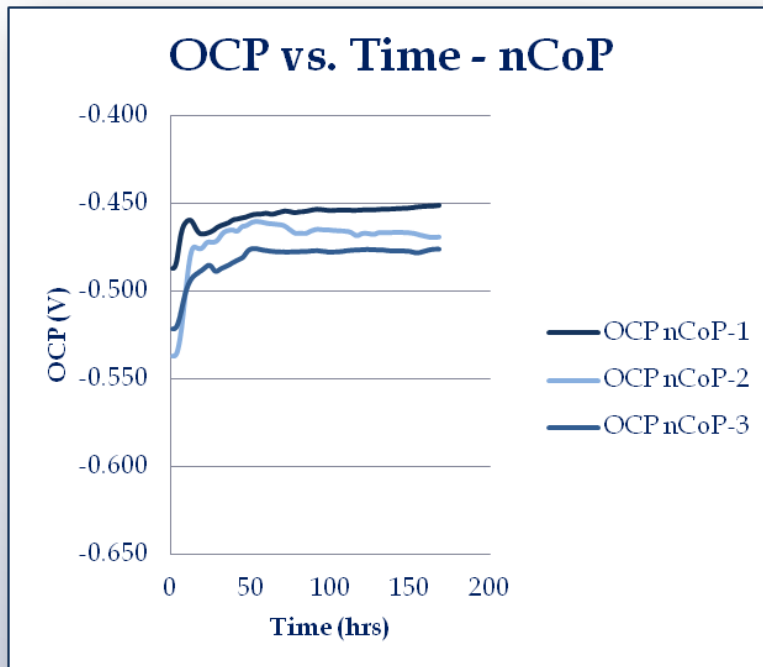
Technical Progress

(Corrosion – Open Circuit Potential)



- AISI 4130 steel coupons
- Environment:
 - 0.5M NaCl, 7 day OCP 1-hr interval
- Reference electrode: SCE
- nCoP shows tendency to reach more noble potentials than EHC

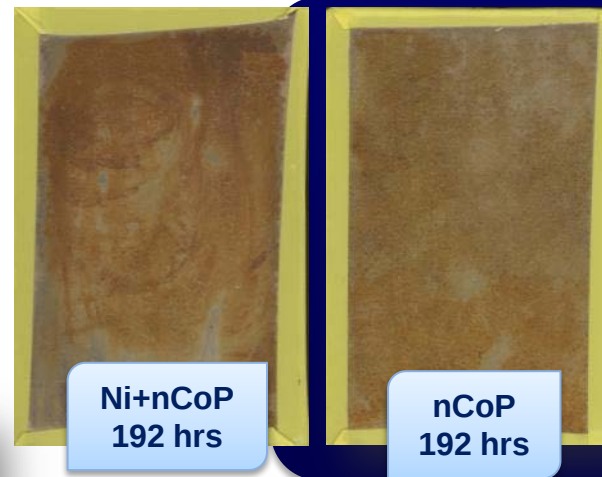
Coating	Mean OCP (mV-SCE)	Final OCP (mV-SCE)
nCoP	-470	-470
EHC	-600	-600



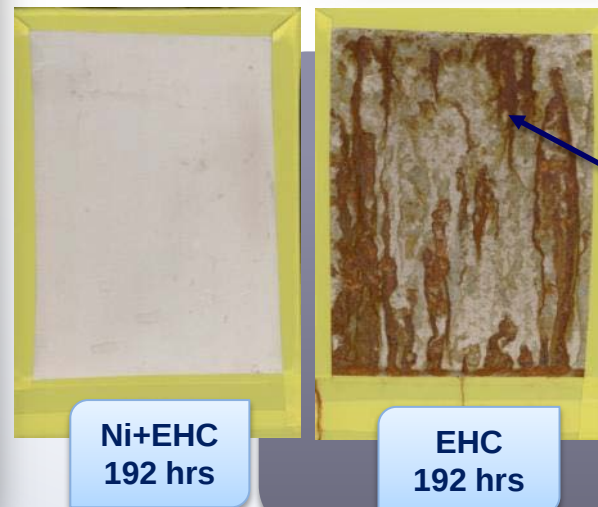
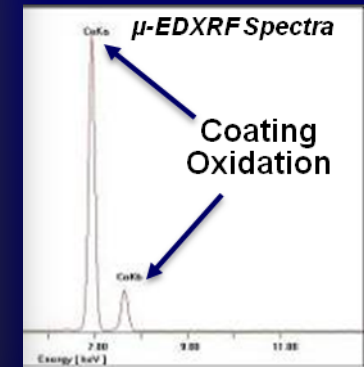


Salt Fog Testing (ASTM B-117)

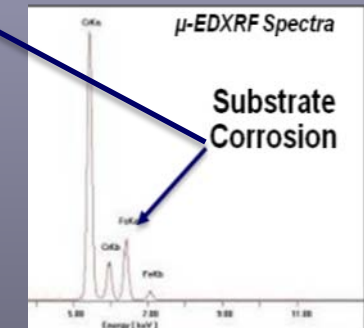
- Test conducted as per ASTM B-117
- Rankings assigned as per ASTM B537
- Major improvement in performance between Ni+EHC and EHC
- No observable difference between Ni+nCoP and nCoP.



Nanovate™ CoP



Hard Chrome





SO₂, Salt Fog Testing (ASTM G85-A4)

- Test conducted as per ASTM G85-A4
- Rankings assigned as per ASTM B537
- Major improvement in performance between Ni+EHC and EHC
- No observable difference between Ni+nCoP and nCoP.

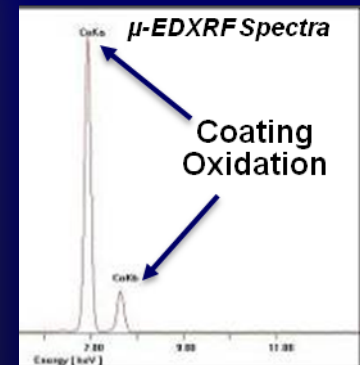


Ni+nCoP
336 hrs



nCoP
336 hrs

Nanovate™ CoP

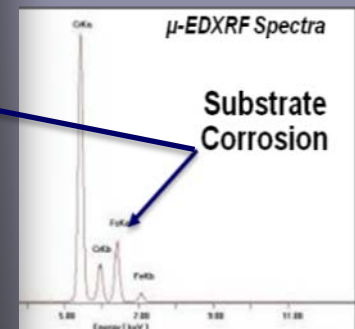


Ni+EHC
336 hrs



EHC
336 hrs

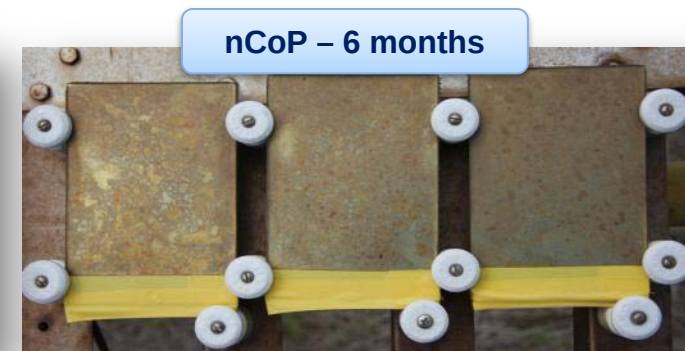
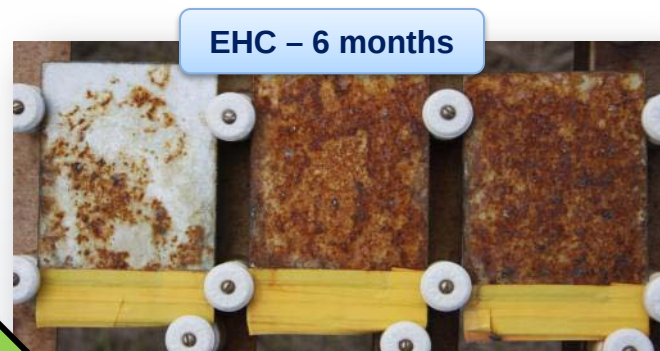
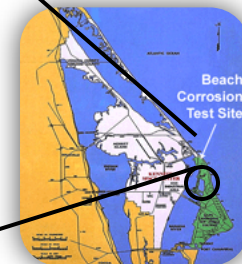
Hard Chrome



Technical Progress

(Corrosion – Beach Exposure)

- Beachside Atmospheric Test Facility, NASA Kennedy Space Center
- EHC exhibits red rust
- No red rust for all other coatings in test to date



OXIDE CHARACTERIZATION

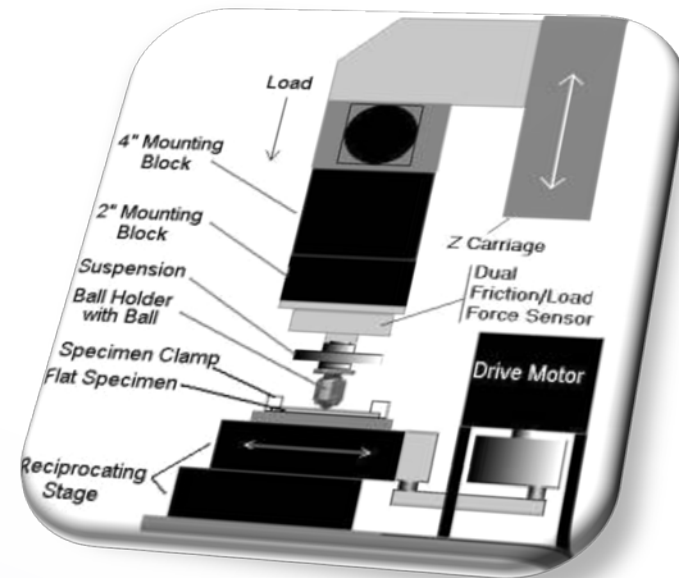
(WHITE PAPER SUBMITTED)

Surface Characterization

- ❑ X-ray photoelectron spectroscopy (XPS) analysis to determine composition of the surface oxide.
- ❑ X-ray diffraction (XRD) analysis to determine presence of oxides or intermetallic compounds.
- ❑ Scanning electron microscope (SEM) to be conducted on mounted cross-section to determine the concentration profiles for Co, Fe and O.

Performance Testing

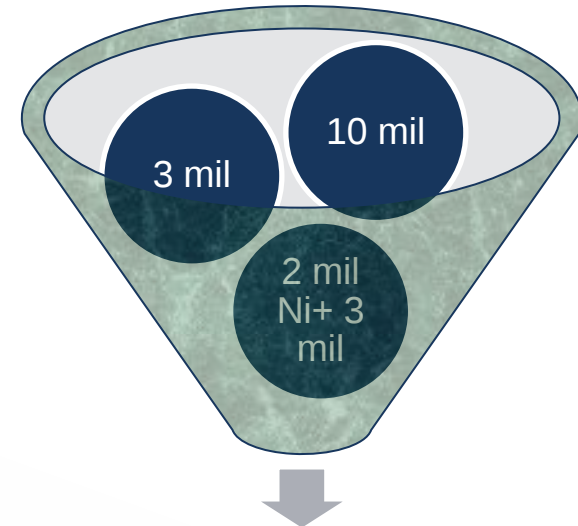
- ❑ Ball-on-flat with linear reciprocating motion (ASTM G133)
- ❑ ambient conditions and simulated salt water solution (i.e., 3.56 wt% NaCl)
- ❑ Mass loss, contact surface profilometry, coefficient of friction and depth profiling (3D imaging)



Axial Fatigue Testing



- 4340 steel (260-280 ksi)
- Shot peened (S110 - 0.008-0.010)
- 16 Ra Minimum
- R ratio: $R = -1$
- Loads: 85% YS to 10^6 Cycles



EHC/NCOP (20 MIL NCOP)

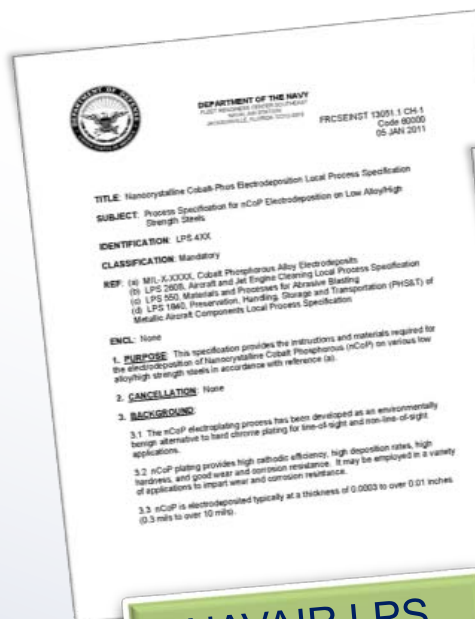




Technical Progress



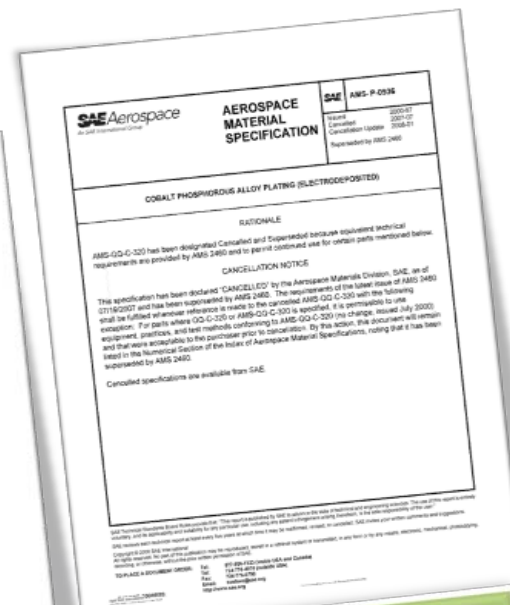
SPECIFICATION DEVELOPMENT



**NAVAIR LPS
(Draft Version)**



**MIL Spec
(MFFP-2011-002)**



**AMS Spec
(Being Pursued)**



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



Project Leader
Integran Technologies, Inc.
416-675-6266 x 375
mahalanobis@integran.com





Backup Material



Technology Transfer



(Extended Stakeholder POCs)



Boeing -
Steve Gaydos



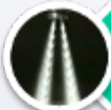
Heroux Devtek -
Nihad Ben Salah



NASA -
Jon Devereaux



UDRI -
Natasha Voevodin



VLN -
William Bloom



Hill AFB -
Dave Frederick



Tinker AFB -
Van Nguyen



Messier Dowty -
Roger Eybel



Boeing Additional Tests

Adhesion

- Chisel
- Flat Peen

Fatigue

- Round Axial
- Flat Axial

Sliding Wear

- Pin-in-Bushing
- Track Roller
- Fretting Wear



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



Coating Properties



Property	Test Method	Applicable Standard	Nanovate CR	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) 600-750 VHN (heat treated)	Min. 600 VHN -
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



Property	Test Method	Applicable Standard	Nanovate CR	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.



Technical Progress



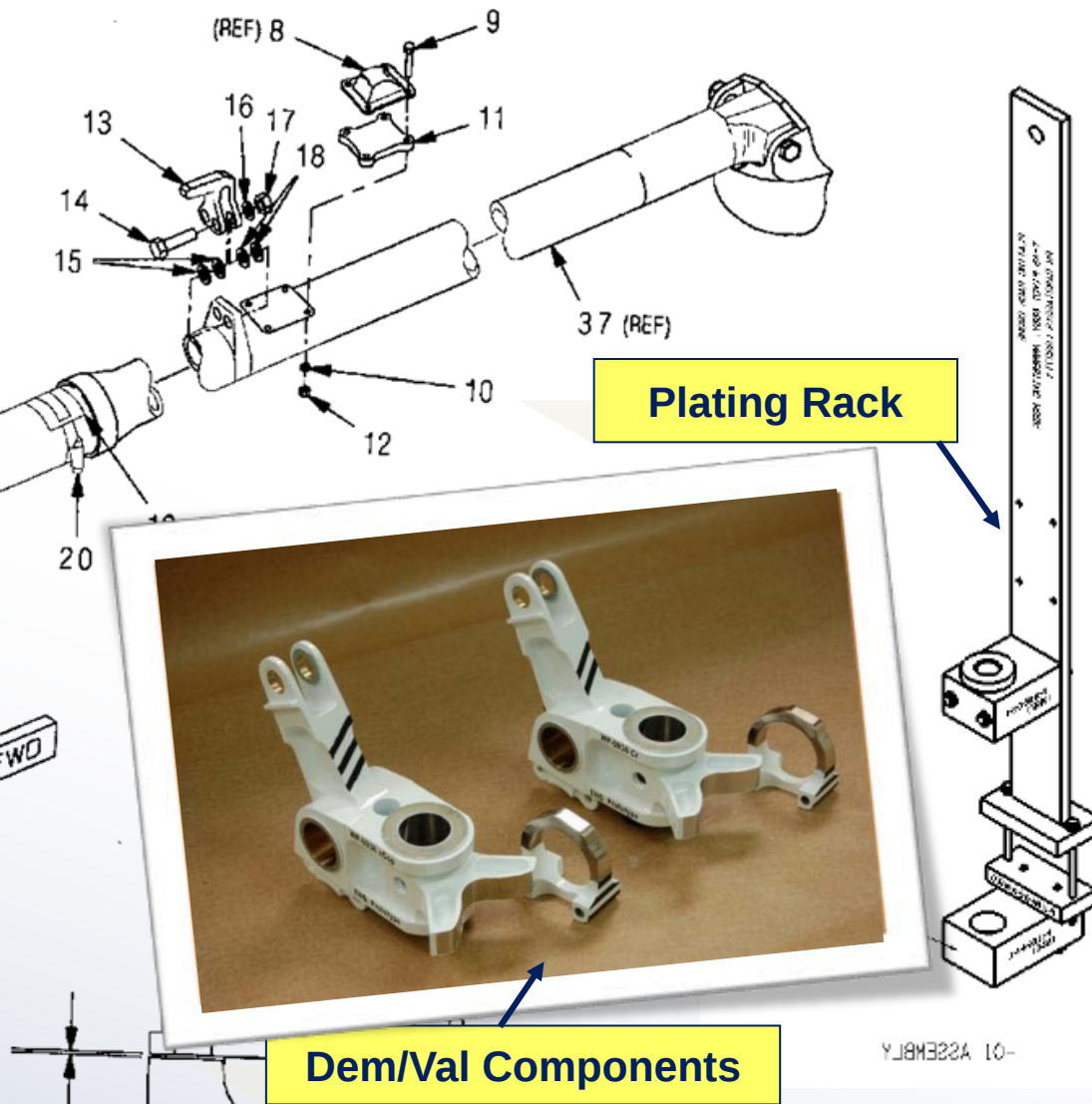
T-45 Pivot Assembly

Plated Area

Plating Rack

Tie Down Ring

Dem/Val Components





Overview of Prior Work



- **SERDP Project PP-1152 (2000 – 2003)**
 - Concept Feasibility
 - **ESTCP Project WP-0411 (2004 – 2007)**
 - Industrial scale-up at Integran
 - Process Line NAVAIR JAX
 - **Supplemental Risk Reduction DOE (2008)**
 - Optimized Plating Parameters
-
- **ESTCP/NESDI Project (2009 – 2011)**
 - ESTCP WP-0936 & NESDI #348
 - JTP/DEM Plan Development
 - Process Development
 - Baseline Dem/Val plated
 - Phase I JTP Tests Completed
 - Elsyca modeling for Dem/Val, fatigue rack optimization



660 gal nCoP Plating tank at Integran

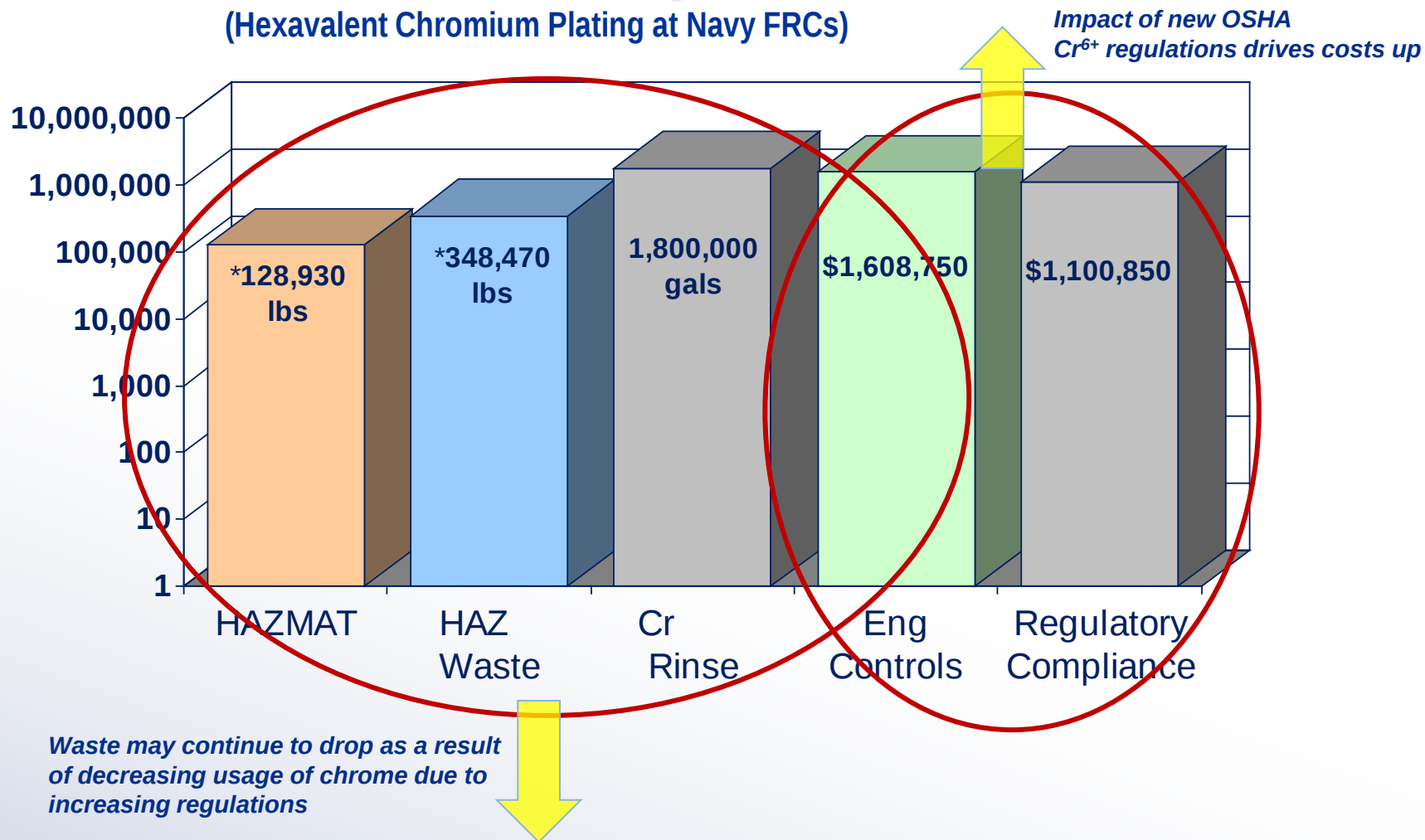


250 gal nCoP tank at FRC-SE



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