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

ESTCP

(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

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
AUG 2012		**00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Nanocrystalline Cobalt-Phosphorous Electroplating as an Alternative to Hard Chromium Electroplating	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	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**36**	

Project Team

NAVAIR:

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

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

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

Dem/Val Tank Pulse Power Supply

Process Line

Activation Tank Power Supply

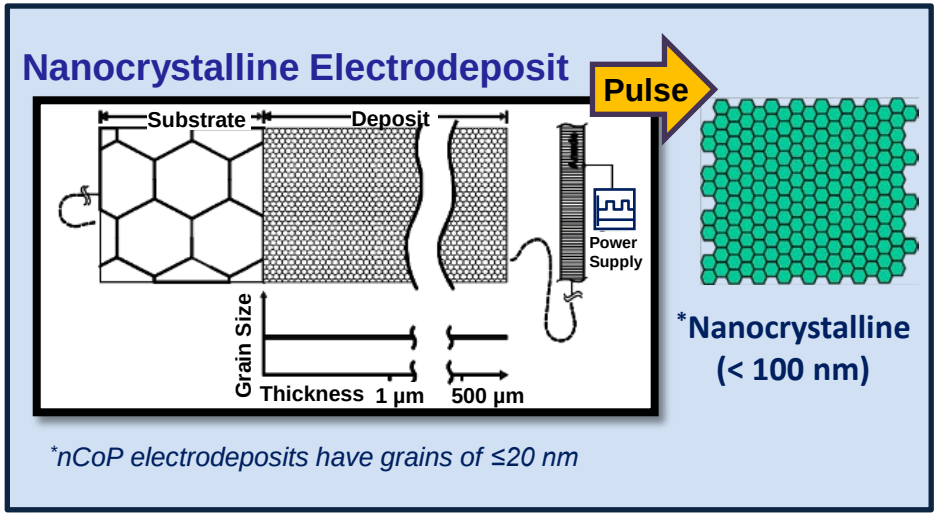
Technical Approach
(Technology Description)

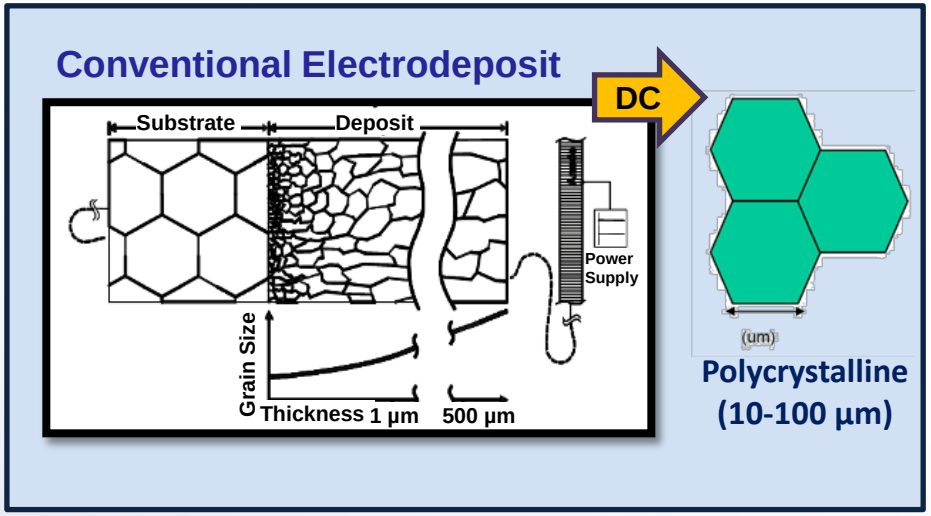
- **Coating applied by electrodeposition**
  - Pulsed Current Waveform Engineering
    - Frequency (Hz) = $1/(t_{on}+t_{off})$
    - Duty Cycle (%) = $t_{on}/(t_{on}+t_{off})x100$

- **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





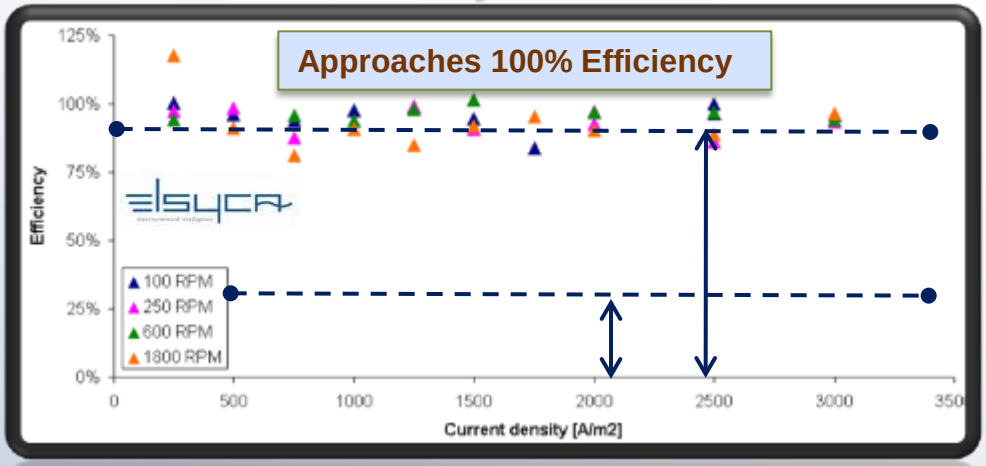
Technical Approach
(Nanocrystalline Co-P Deposits)

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



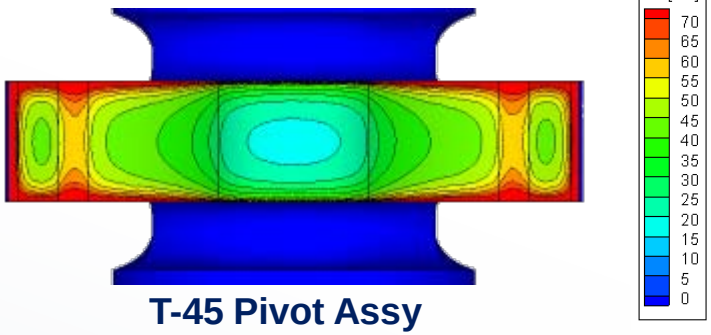
Nanovate CoP

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 in², <5 pits/30 in²	**Pass** ≤ 1 spot per 30 in²	**Pass** ≤ 5 spot per 30 in²

Chemical Strip Demonstrated

Demonstrated on T-45 Pivot at JAX

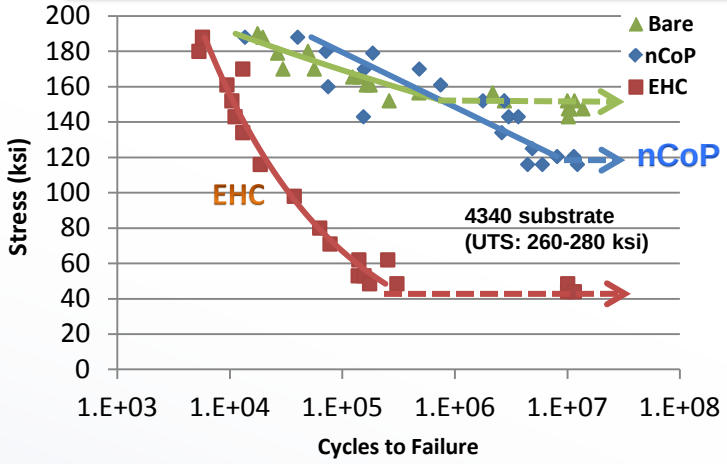
Plated Pivot

Stripped Pivot

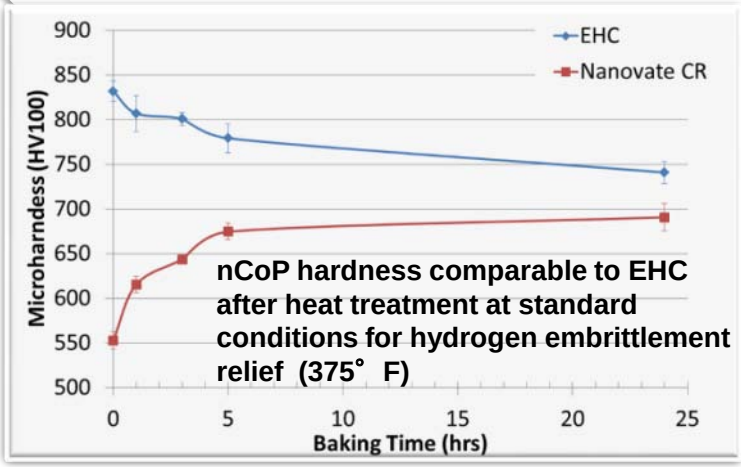
Masking Evaluation/Downselect

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

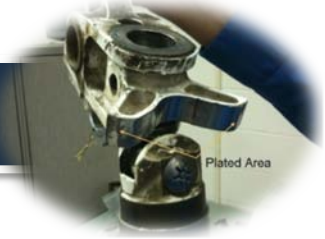
NAVAIR JAX Base line Plating - Dem/Val

EHC Plating of T-45 Pivot Assy

Technical Progress

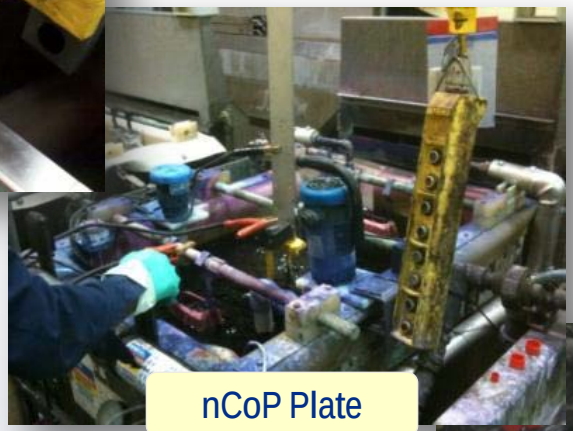
(Component Dem/Val Plating)

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

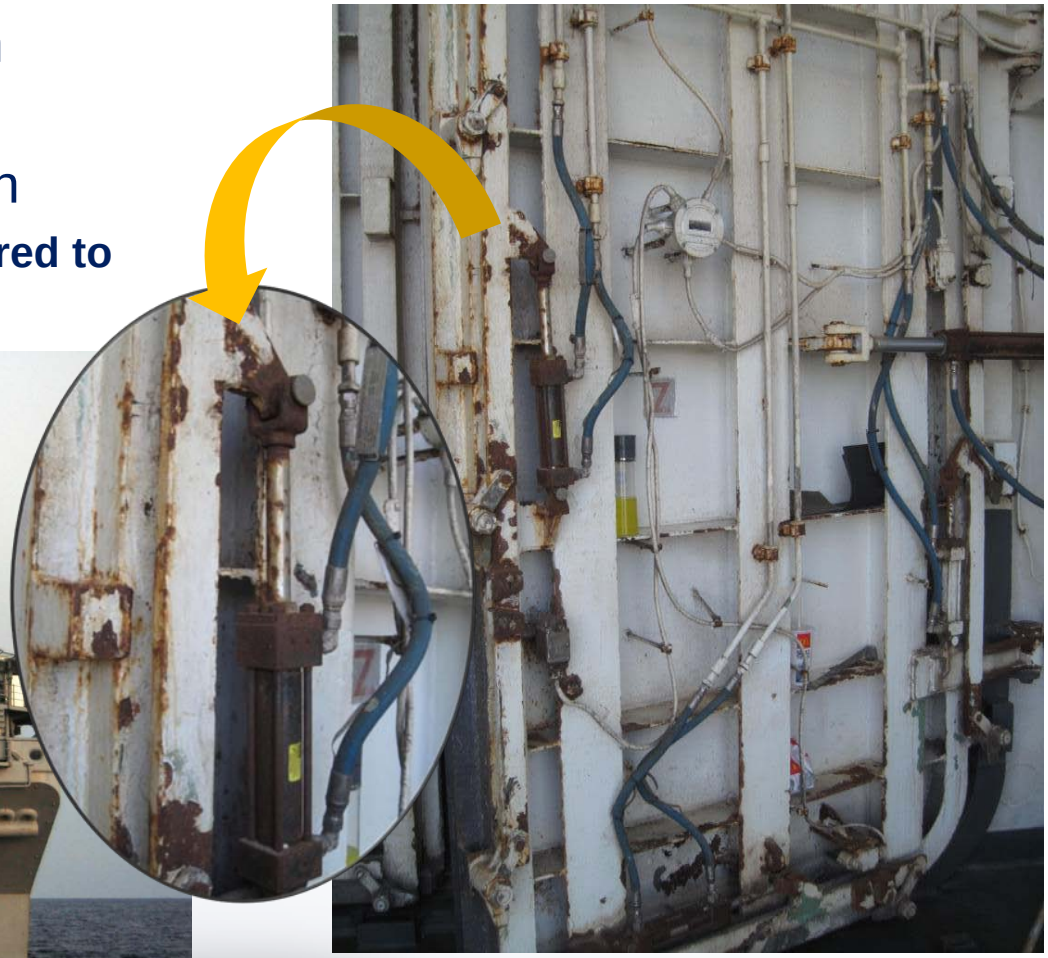
Technical Progress

(NAVSEA Dem/Val Component Identified)

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



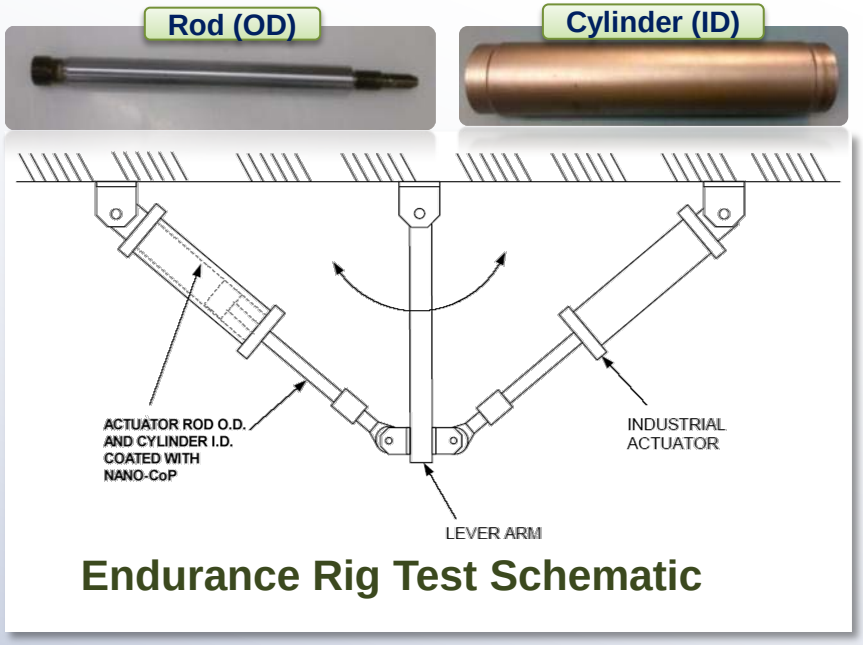
Stern Gate Piston Shaft

Technical Progress
(Endurance Rig Testing)

Messier-Dowty
SAFRAN Group

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		

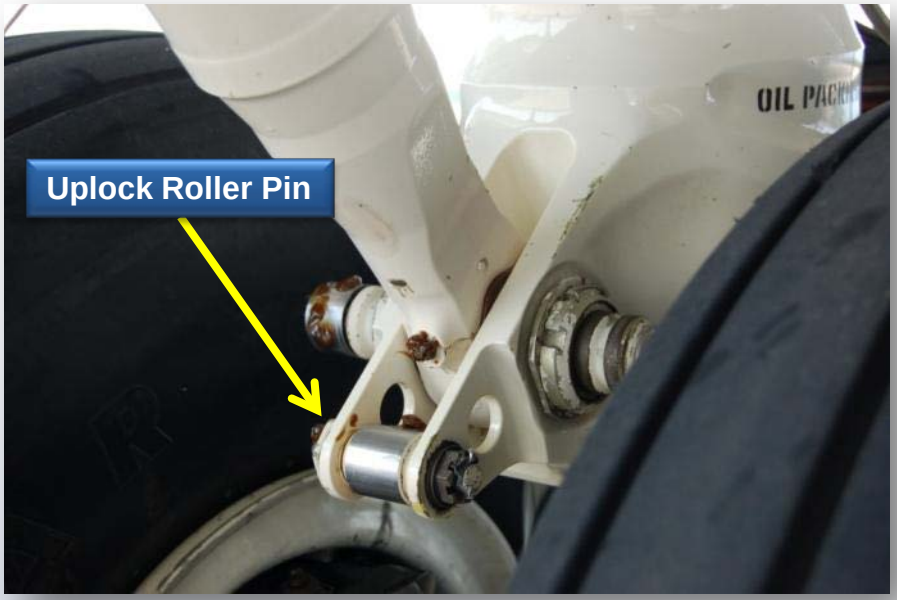
**$121K In kind funding (Messier-Dowty)*

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

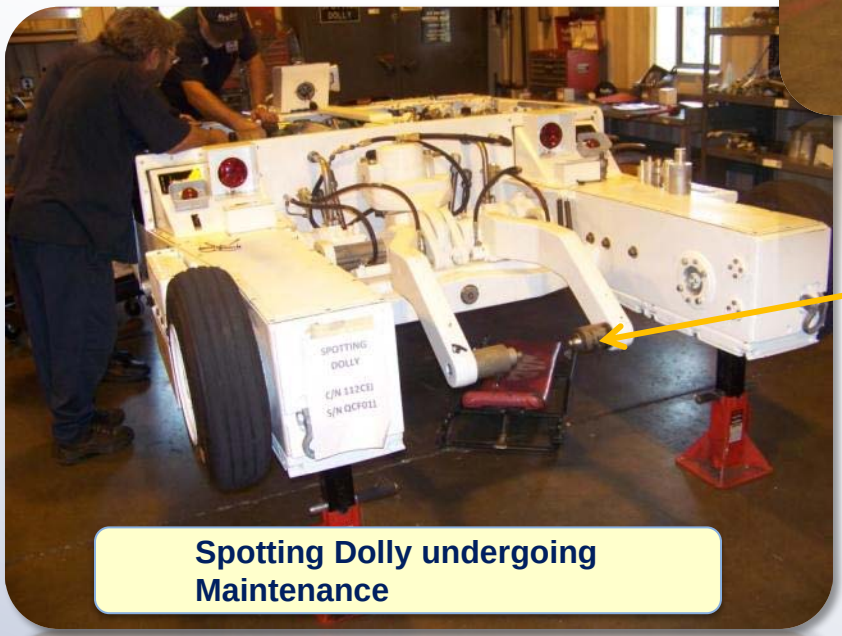
nCoP Plated Uplock Roller Pins

Technical Progress

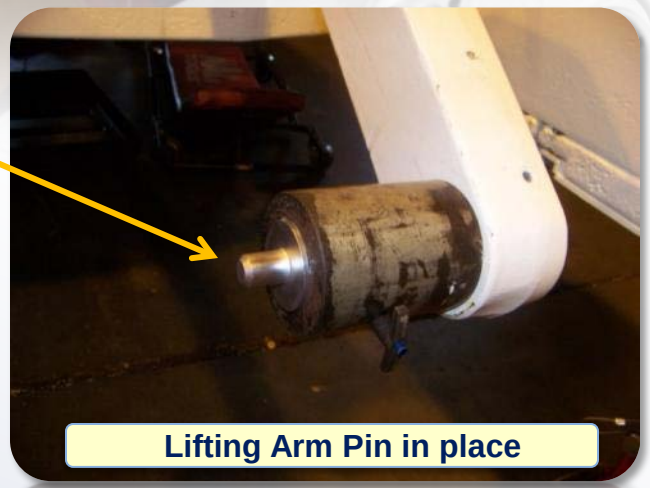
(Spotting Dolly Lifting Pin)

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

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**

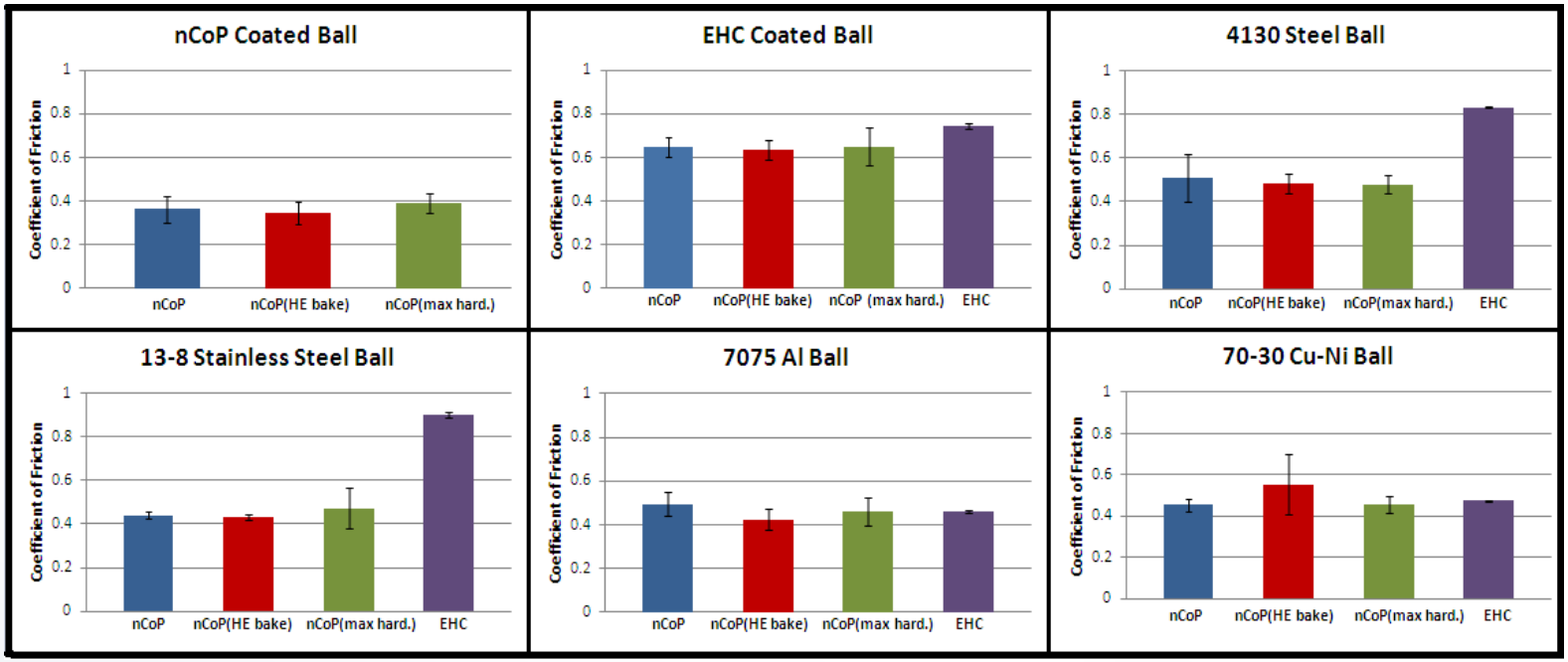
**EHC samples showed some form of minor attack. However, it did pass according to JTP acceptance criteria.*

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 ≤ 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

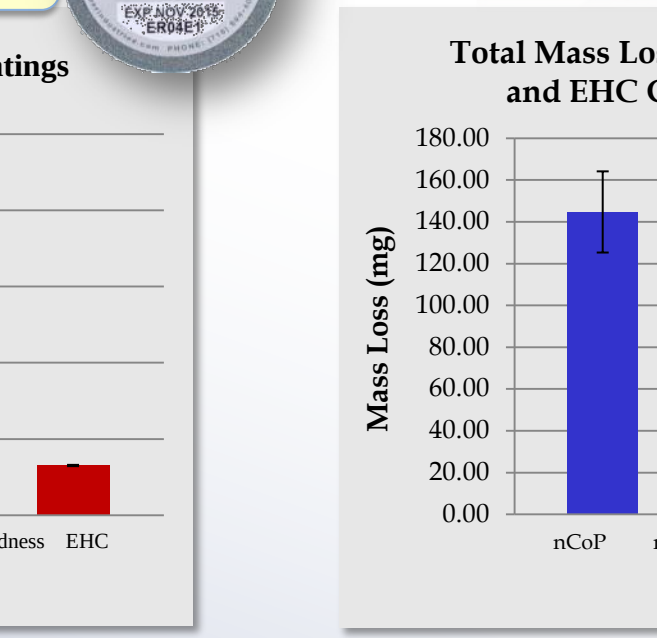
*** Does not include nCoP ball on EHC results**

Technical Progress

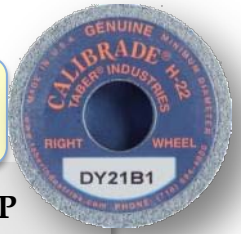
(Abrasive Wear)

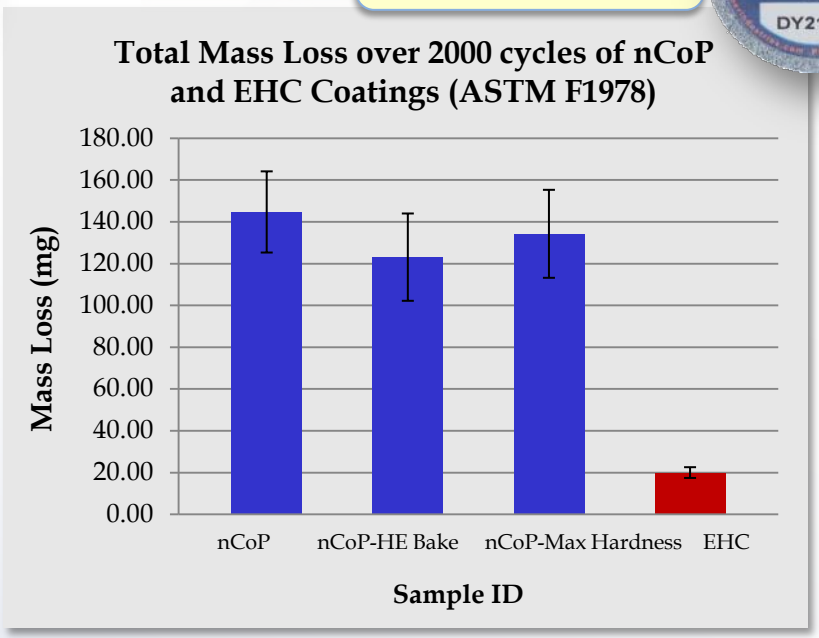
- Taber wear testing to assess abrasive wear resistance of coatings
- Performed ASTM D4060
- Performed ASTM F1978

• CS-17 wheels
• 1000g load



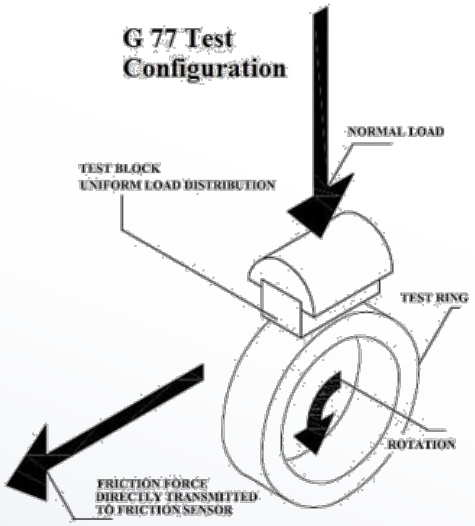
• H-22 wheels
• 250g load

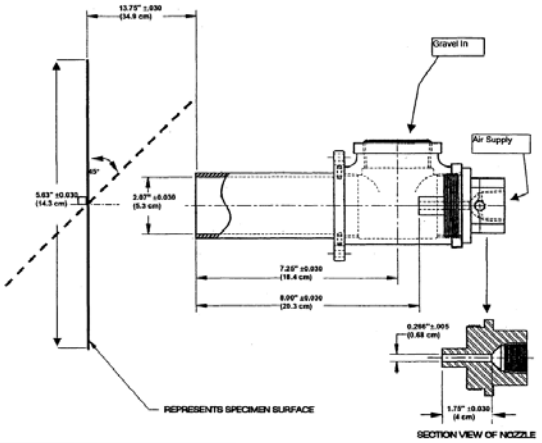


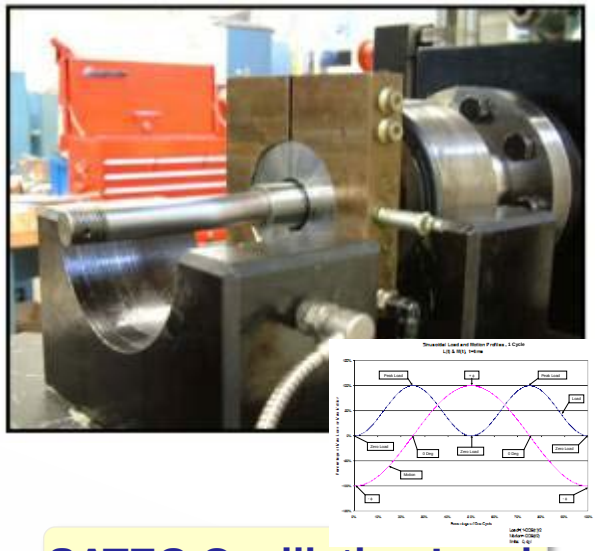


Technical Progress

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

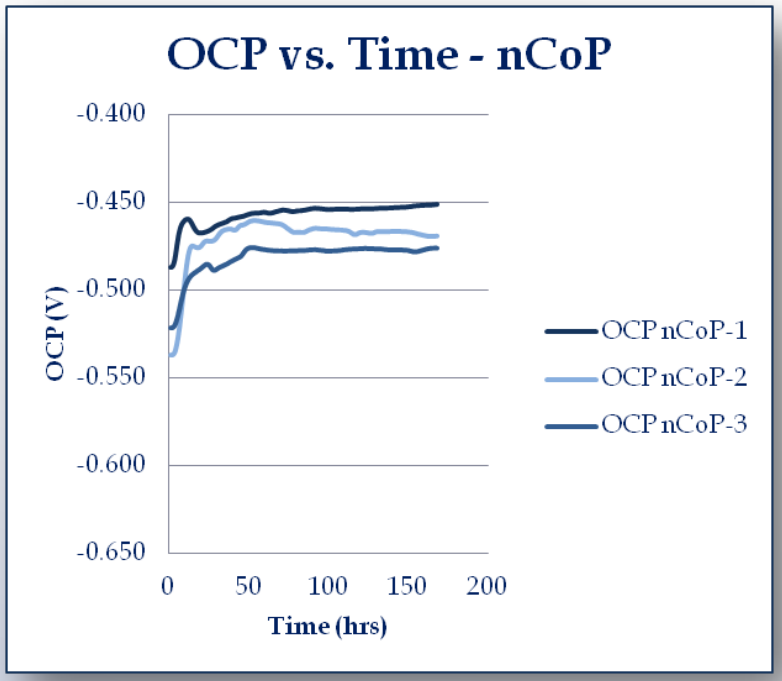
- Boeing Specific Test
- Pin/Bushing Oscillating Wear Test
- Constant/ Sinusoidal load-motion profile

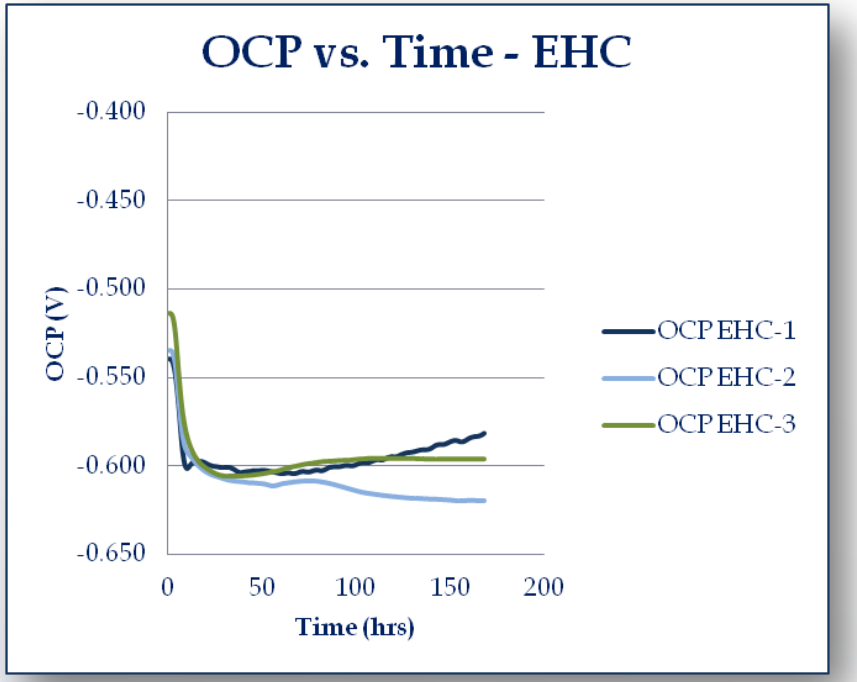
Technical Progress

(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



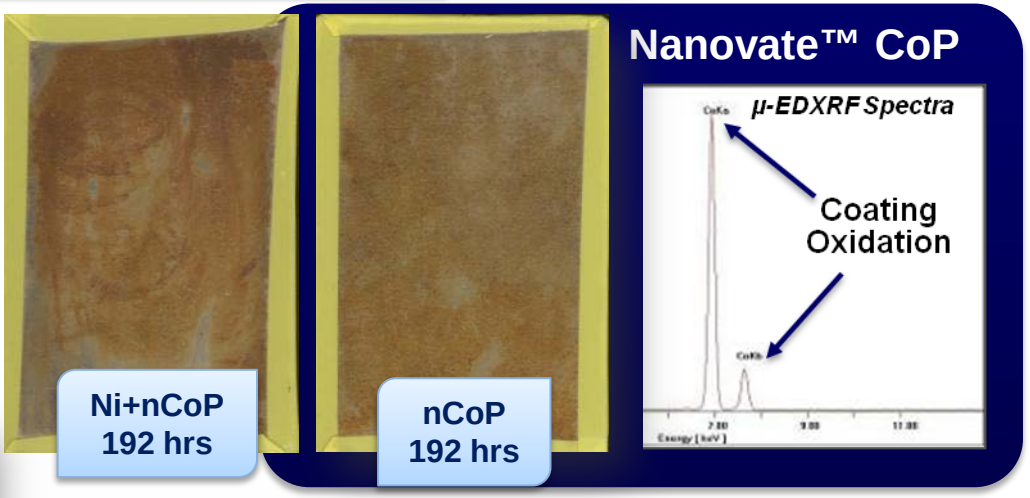


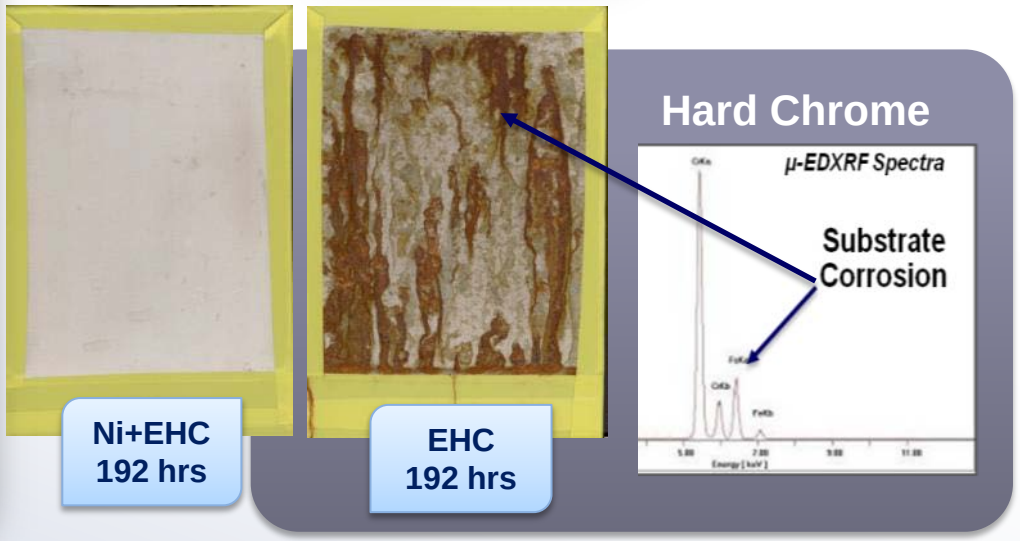
Technical Progress

(ASTM B-117 Corrosion Testing)

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.





Technical Progress

(ASTM G85-A4 Corrosion Testing)

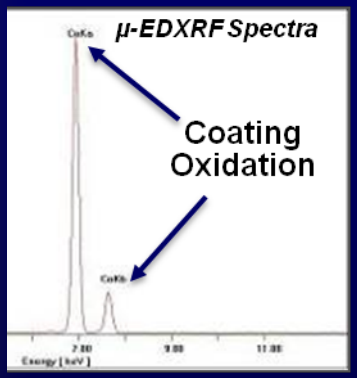
SO2, Salt Fog Testing (ASTM G85-A4)

- 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

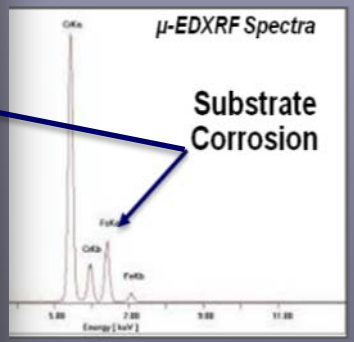
Nanovate™ CoP



Ni+EHC
336 hrs

EHC
336 hrs

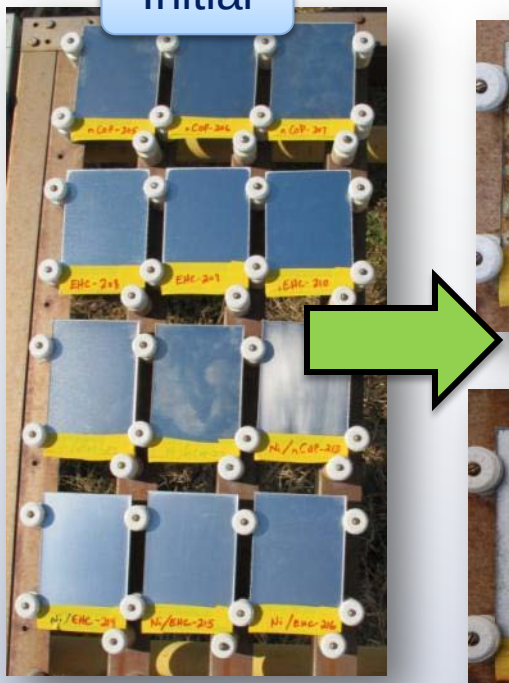
Hard Chrome

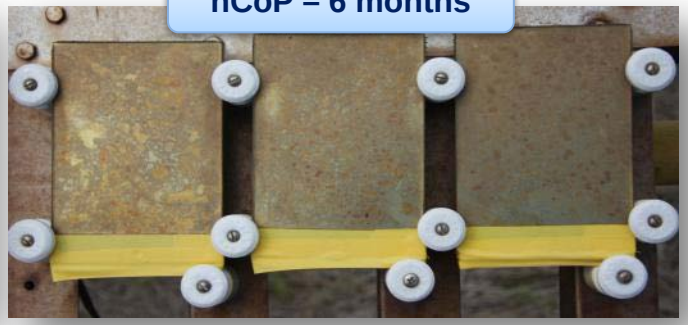


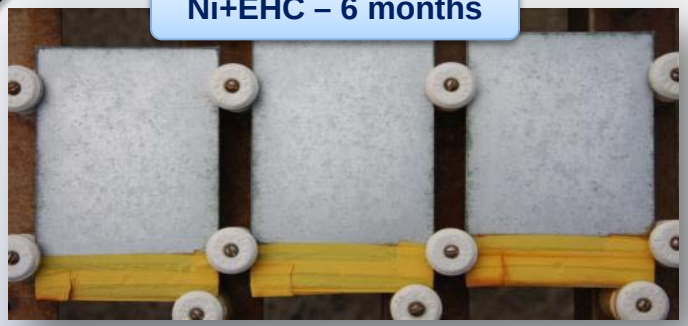
Technical Progress

(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







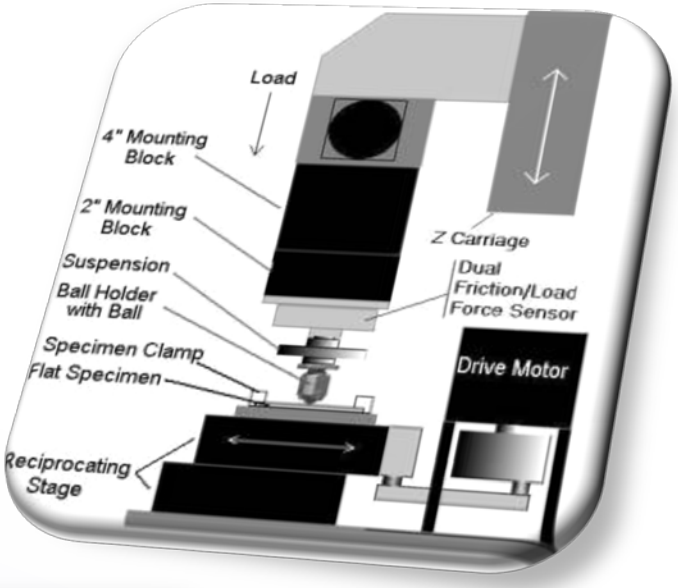
OXIDE CHARACTERIZATION
(WHITE PAPER SUBMITTED)

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.

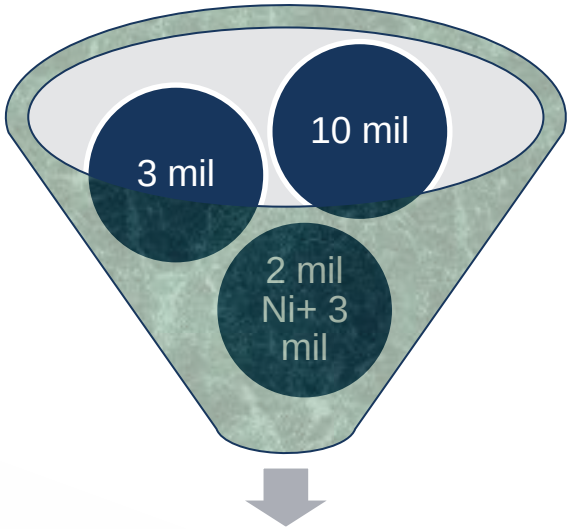
Performance Testing

- ❑ 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

BOEING

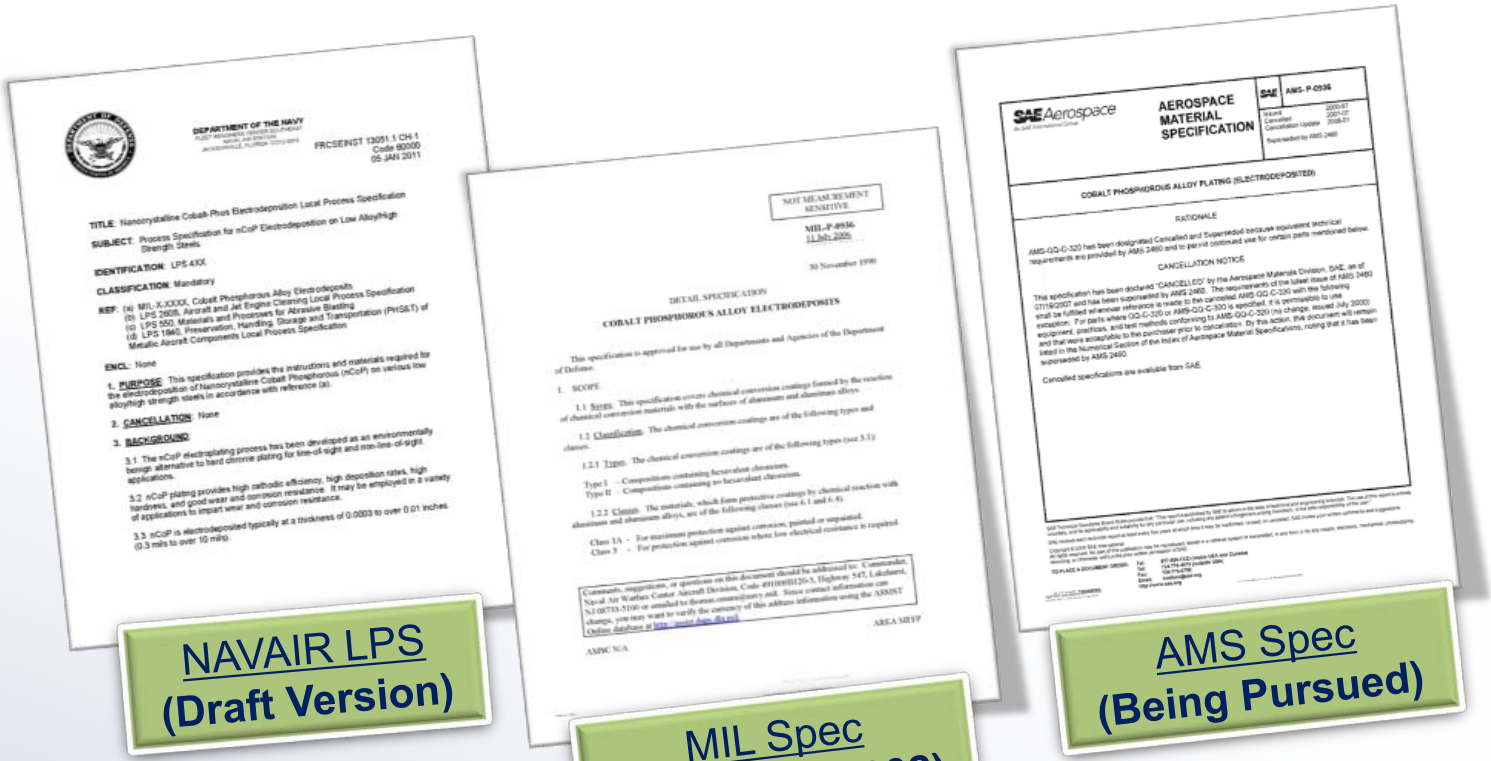


EHC/NCOP (20 MIL NCOP)

- 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

Technical Progress

SPECIFICATION DEVELOPMENT



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

BOEING


Heroux Devtek -
Nihad Ben Salah

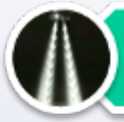
HEROUX DEVTEK


NASA -
Jon Devereaux

NASA


UDRI -
Natasha Voevodin

UDRI
UNIVERSITY of DAYTON RESEARCH INSTITUTE


VLN -
William Bloom

VLN


Hill AFB -
Dave Frederick


Tinker AFB -
Van Nguyen


Messier Dowty -
Roger Eybel

Messier-Dowty
SAFRAN Group

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 Il, 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

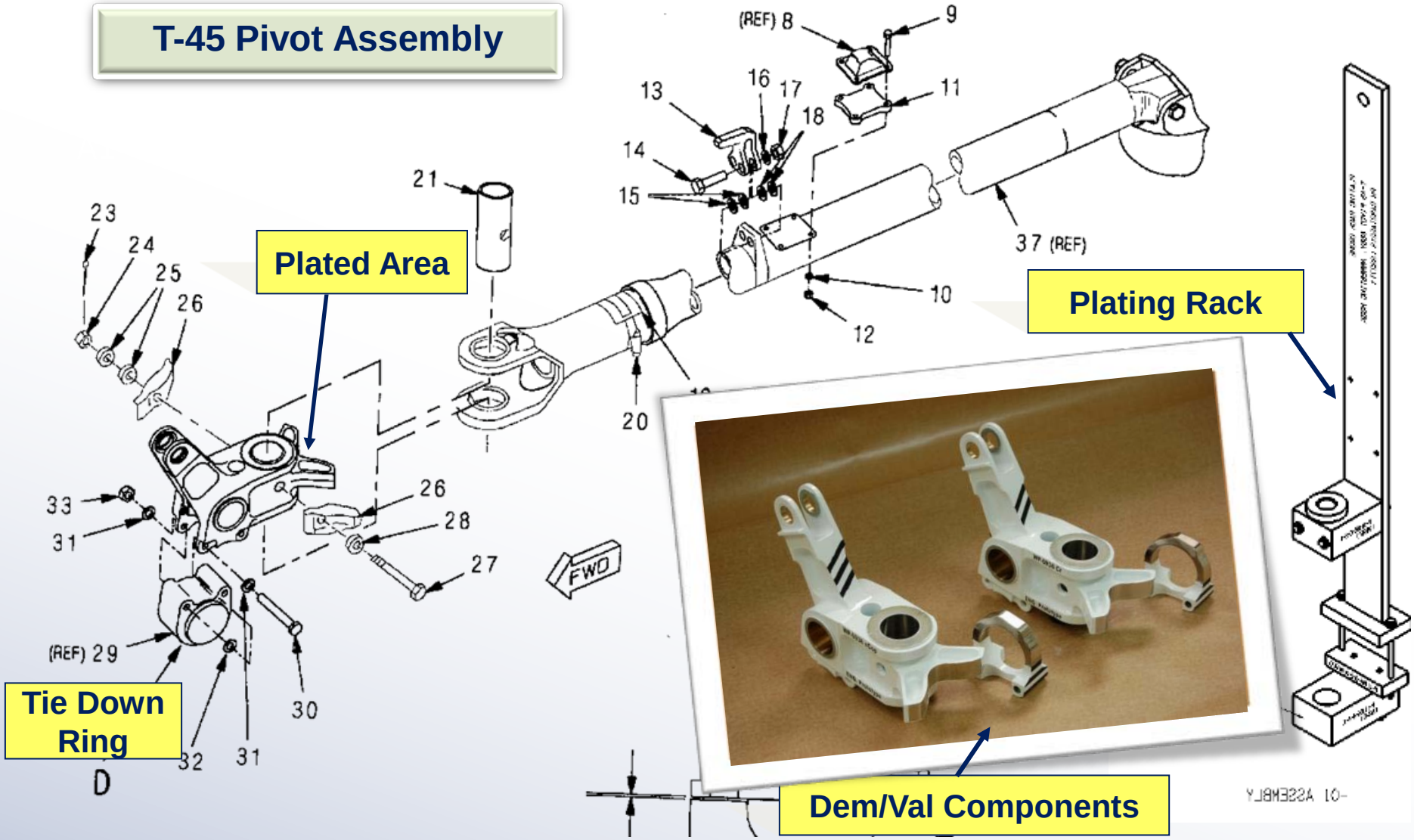
Property	Test Method	Applicable Standard	Nanovate CR	EHC
Appearance and porosity	Visual and microscopic inspection	N/A	Free from pits, microcracks and pores	Microcracked
Grain Size	X-Ray Diffractometry	N/A	8-15 nm	-
Hardness	Vickers Microhardness	ASTM B578	550-600 VHN (as-deposited) 600-750 VHN (heat treated)	Min. 600 VHN -
Ductility	Bend Test	ASTM B489	2-7%	<1%
Adhesive Wear	Pin on Disc (Al_2O_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



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

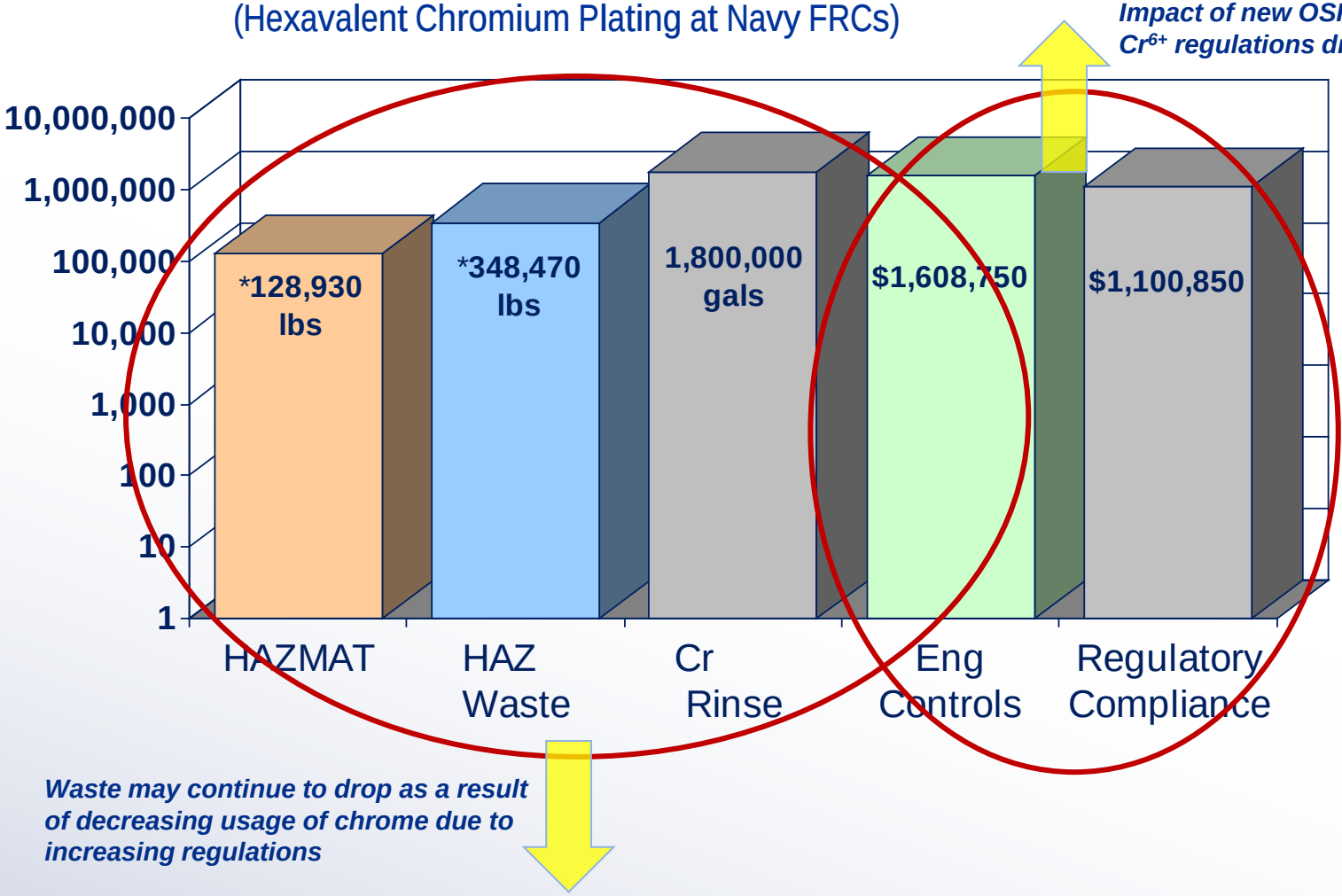
660 gal nCoP Plating tank at Integran

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