Some Properties of Electroless Nickel, Hard Chromium, HVOF Spray

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Data collected from a variety of sources, including The Properties of Electroplated Metals & Alloys by Lowenheim

Photos & video by F. Altmayer

Electroless Nickel-P (ASTM B733)

Type I: (No %P specified)

Type II:

- 1-3%P
- Microcrystalline structure
- High solderability, bondability, electrical conductivity
- Resistant to strongly alkalis

Type III:

- 2-4% P
- Microcrystalline structure
- High as-plated hardness (620 to 750 KHN_{100}), excellent wear

Type IV:

- 5-9%P
- Amorphous structure
- Most commonly deposited
- Good wear and corrosion resistance

Type V:

Type IV EN Plated Aerospace Battery Cap

Type V EN Plated Strainer

Photos by F. Altmayer

Electroless Nickel-B (ASTM B607)

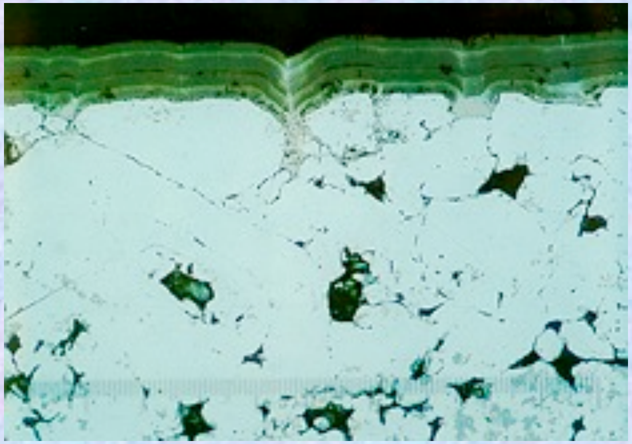
- Columnar, micro-porous structure
- Poor corrosion protection unless lubricated

"Type 1" (0.1 to 3.5%B):

- **Produced from amine-borane solutions**
- **Most suitable for wire bonding and soldering**
- **Typically not heat treated for higher hardness**

Electroless Nickel

EN is more noble than the substrates it is plated upon (most cases)
Corrosion resistance depends on thickness, surface finish and level of porosity



EN over Powder Metallurgy Part

ASTM B-733 EN Thickness

Service Conditions	Min. Thick. (microns)	Min. Thick. (mils)
SC0 Minimum Service • Lubricated wear • Electronics diffusion barrier	0.1	0.04
SC1 Mild Service • Light wear • Indoor Protection	5	0.2
SC2 Moderate Service • Moderate wear • Industrial Atmosphere	13	0.5
SC3 Severe Service • Severe wear • Seawater, etc.	25	1.2
SC4 Very Severe Service • Aggressive environment	75	2.4

Economics:

- 6-8 X as expensive as electroplated Ni
- Overall finishing cost of a part may be lower vs. hard chromium due to elimination/reduction of post plate grinding/polishing

Electroless Nickel

Adhesion

As Plated:

Steel:

bond strength = 400 Mpa (60 ksi)

Stainless steel:

bond strength ~ 140 Mpa (20 ksi)*

Copper/Alloys:

bond strength = 300 to 350 Mpa (40 and 50 ksi)

Aluminum/Alloys:

bond strength = 300+ Mpa (40 ksi)

Titanium/Alloys:

bond strength = 100 Mpa (14 ksi), unless thermally treated

Diffusion Treatments:

Steel:

2-4 hour @ 180-200°C

Stainless steel:

1 hour @ 275-300°C

Copper/Alloys:

1 hour @ 150-200°C

Aluminum/Alloys:

1 - 4 hours @ 120-150°C

Titanium/Alloys**:

2 hours @ 480°C

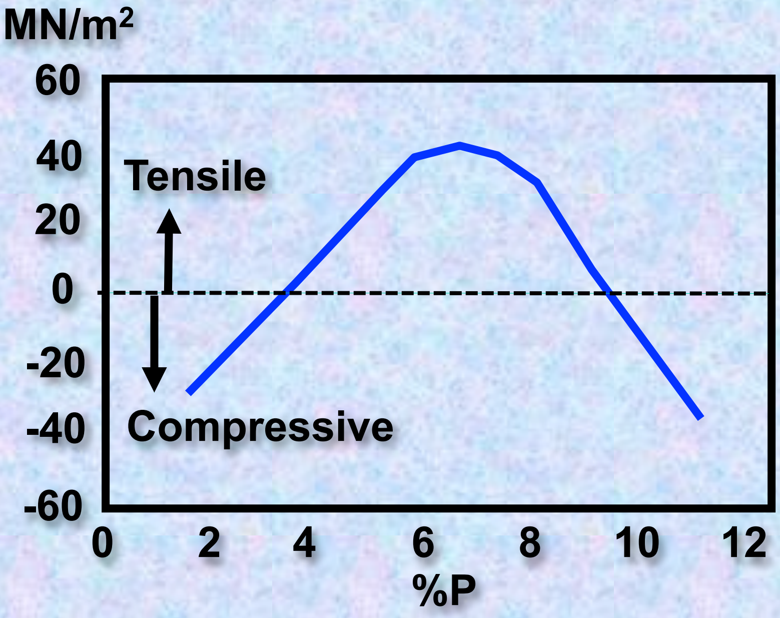
***Anodic etch of stainless steel alloys in a Woods nickel strike before EN plating can increase the adhesion to 510 Mpa (68ksi)**

****ASTM B733 suggests thermal treatment on Ti 1-4 hours at 300-320°C. This is contradicted by US Pat. 4,414,039 which claims no improvement below 400°C**

Electroless Nickel

Internal Stress

High levels of internal stress will reduce EN-P ductility, increase porosity and decrease corrosion resistance

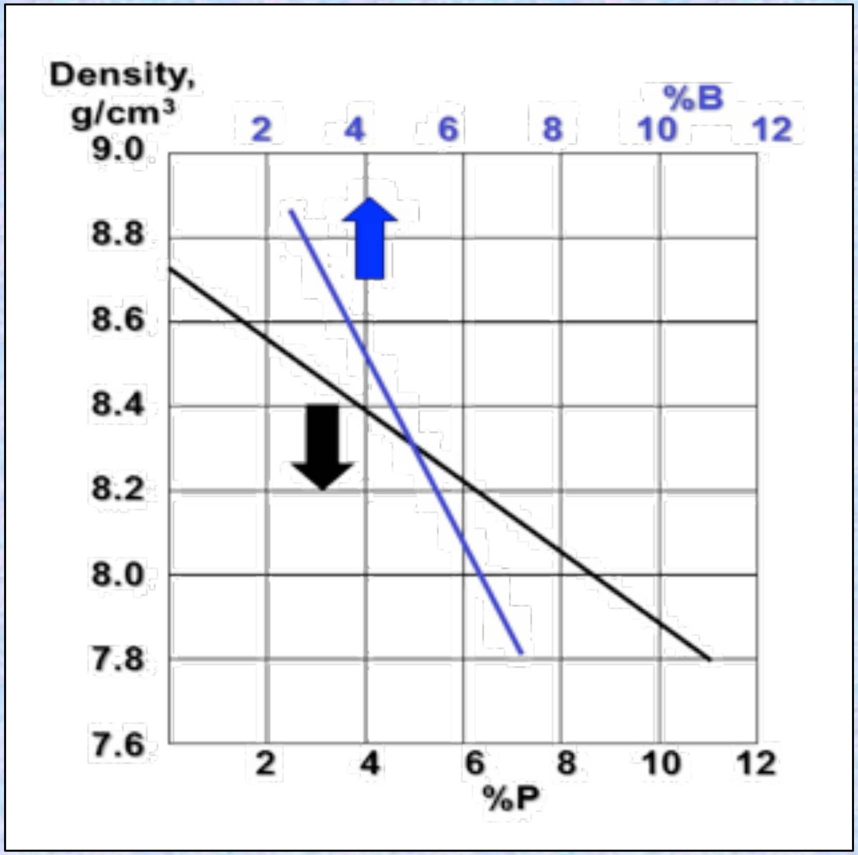


Sources:

- Thermal expansion differences, coating v. substrate
- Non-homogenous deposit cause by:
  - High concentration of complexing agents
  - High concentration of orthophosphite
  - Metal contaminants
    - Bi > 5 ppm = ~50,000 psi tensile
    - Sb > 5ppm = ~50,000 psi tensile
- Heat treatment (above 220°C/420°F) = 4 to 6% shrinkage, increasing tensile stress

Note: 1 MN/m^2 = 145 psi

Electroless Nickel



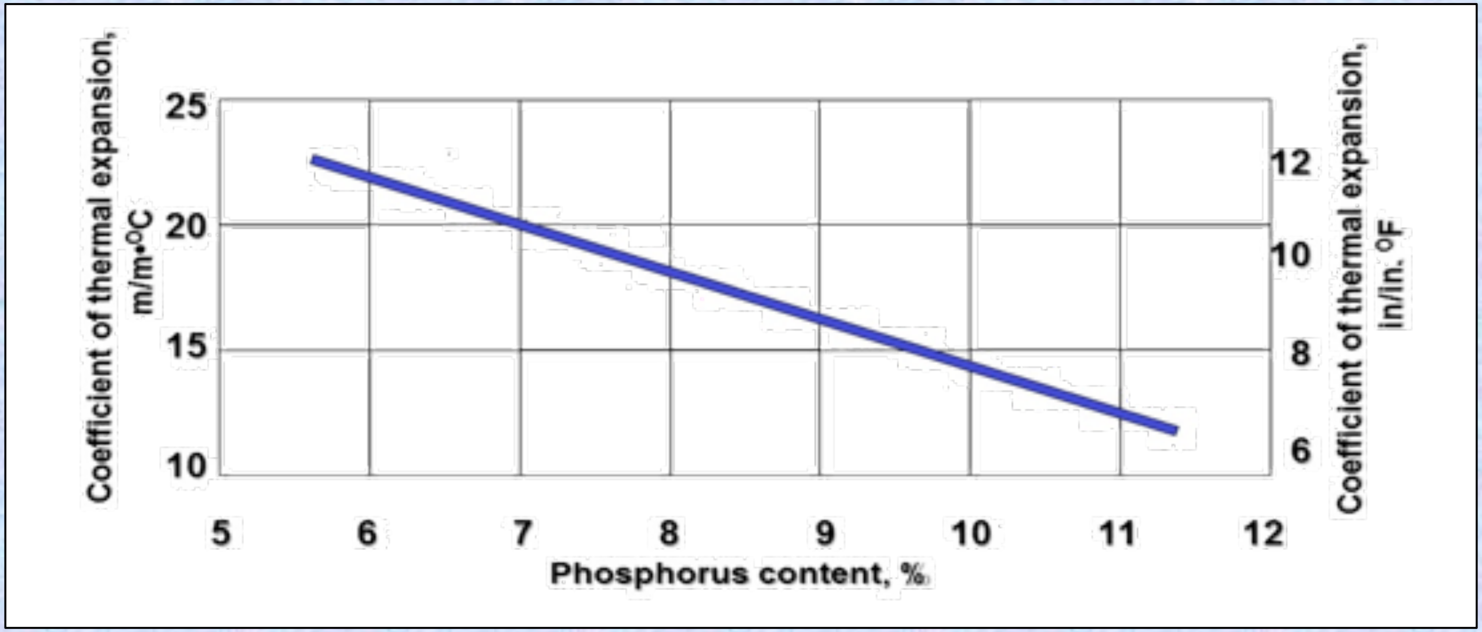
Density of the Deposit:

- Varies with %P or %B in deposit
- Can impact thickness tests
  - Thickness testing devices typically depend on a known density [T = W/(d x a)]
  - Match calibration standard to deposit composition

Electroless Nickel

Thermal Expansion:

- Matches well with steel
- Highly dependent on %P:

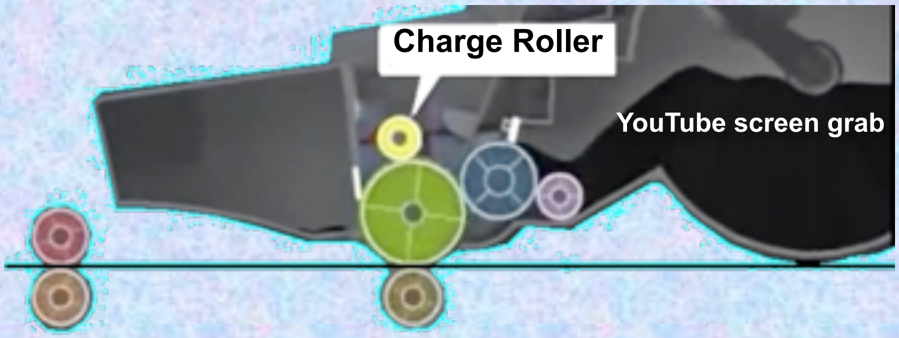


Electrical Conductivity:

- ~60-800μohm-cm, depending on %P and solution composition
- Heat treatments can increase conductivity 3-4X

Electroless Nickel

Magnetic Properties



EN plated aluminum charge roller in a laser cartridge must be non-magnetic

*** Note:** A poly-alloy containing 5-7%P + ~4%Mo = 0 Oersteds, 0 Gauss

Coercivity (Oersted):

"Intensity of magnetic field that must be applied to de-magnetize a metal once it has been placed into and removed from a magnetic field"

As Plated:

- 3.5% P = 30 Oersteds
- 7-8%P = 1.4-2.0 Oersteds*
- >10% = 0 Oersteds

After Heat Treatment:

- 100-300 Oersteds

Electroless Nickel

Magnetic Properties

Remnant Flux (Gauss):

“Intensity of the magnetic field remaining in a metal after an external magnetic field has been applied and removed”

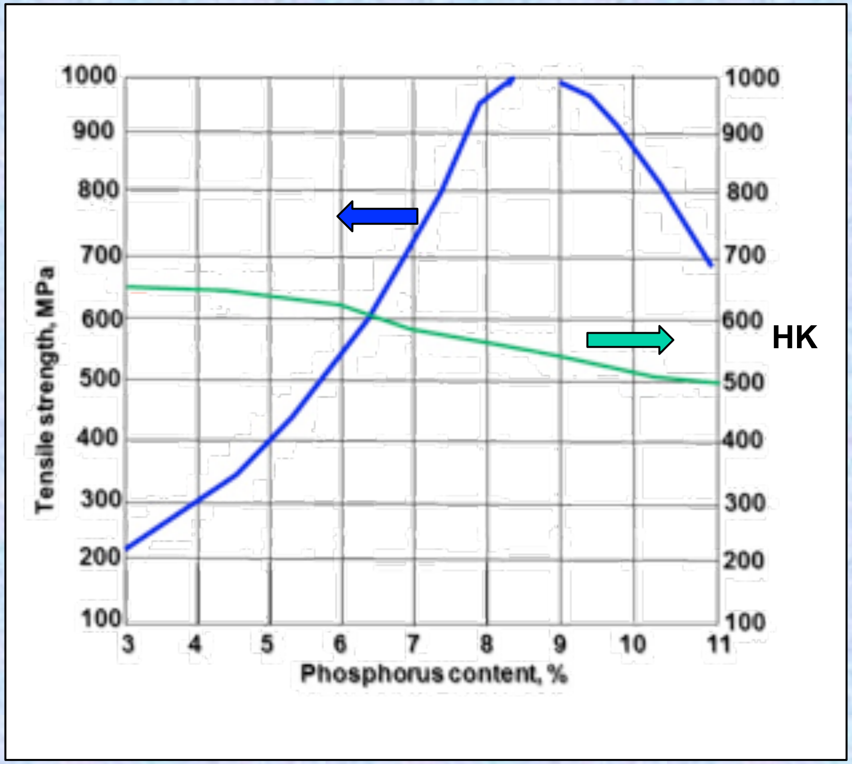
As Plated:

- **0-1000 Gauss (depending on %P)**

After Heat Treatment:

- **1000-3000 Gauss for normally deposited Ni-P alloys**
- **<100 Gauss can be achieved by alloying and or stress manipulation**

Electroless Nickel



Tensile strength and As Plated Hardness vs. %P

Tensile Strength/Elongation:

- 1-3%P = 150-200MPa/<1%
- 5-7%P = 420-700MPa/<1%
- 7-9%P = 800-1100MPa/1%
- 10-12%P = 650-900MPa/1%

Ductility:

- Treatments up to 400°C = reduced strength/ductility
- Treatments >400°C improve ductility/elasticity, reduce hardness

Modulus of Elasticity:

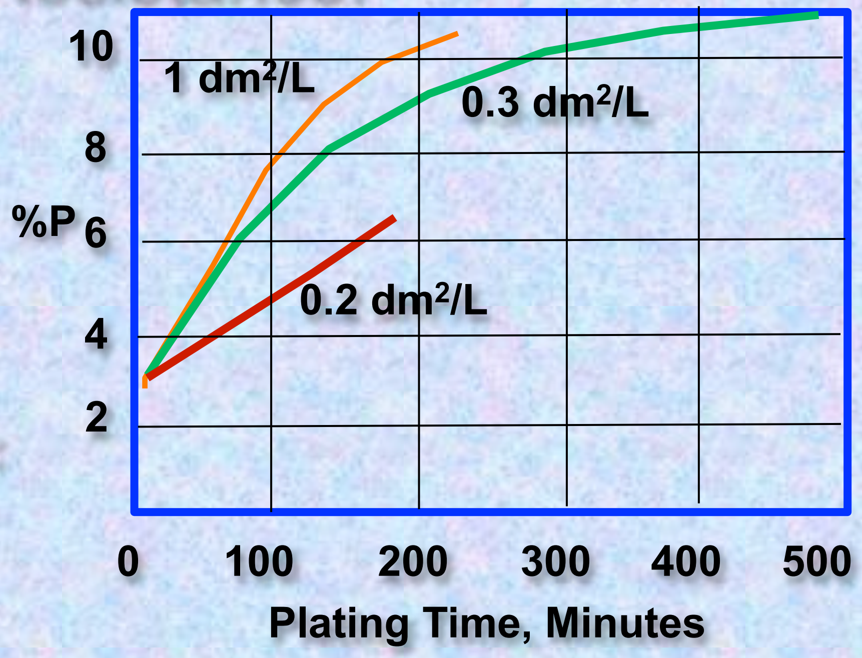
- 7 – 8%P = 120 GPa (18 x 10^6psi)
- 10 – 11%P = 200 GPa (28 x 10^6 psi)
- Heat treating @ >200°C, (400°F) increases the modulus of elasticity

Electroless Nickel

Corrosion Resistance:

Corrosion Resistance:

- **Proportional to %P**
  - **> %P = >corrosion resistance**
- **Impacted by impurities**
- **Impacted by surface roughness**
- **Impacted by heat treatment**



Corrosion Rates (mils/yr. for 9%P):

3% NaCl:	0.04
DI water:	nil
Distilled water:	0.29
Beer:	0.0078
Gasoline:	0.0022
Ammonium sulfide:	0.15*
Lactic acid:	0.145*
Perchlorethylene:	0.15*

Impact of low tank loads on %P

***Not compatible**

Electroless Nickel

Corrosion Resistance:

Heat Treatment vs. Corrosion Resistance

In 10% HCl at 25°C

Heat Treatment	Hardness, VHN_{100}	Corrosion Rate µm/y	Corrosion Rate mpy
None	480	15	0.6
190°C (375°F) for 1½ hours	500	20	0.8
290°C (550°F) for 6 hours	900	1900	75
290°C (550°F) for 10 hours	970	1400	55
340°C (650°F) for 4 hours	970	900	35
400°C (750°F) for 1 hour	1050	1200	47

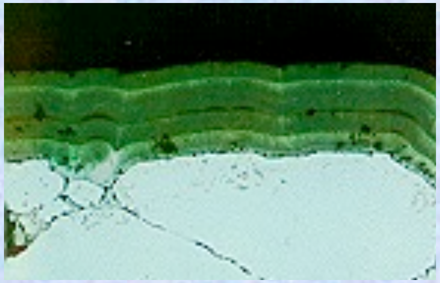
Impurities vs. Corrosion Resistance:

*CO_2 saturated, 3½ percent salt brine at 95°C (200°F).

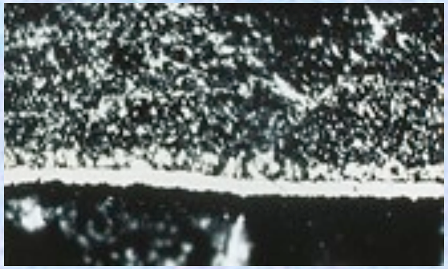
%P	% Impurities	Corrosion Rate* µm/yr	Corrosion Rate* mils/yr
10.2	trace	5	0.2
11.8	0.04 Sn	7	0.3
8.3	0.05 Cd	24	0.9
10.3	0.12 Pb	15	0.6
8.0	0.13 S	15	0.6
10.4	0.05 Pb & 0.08 Cd	11	0.4

Heat Treating EN for Hardness

Before

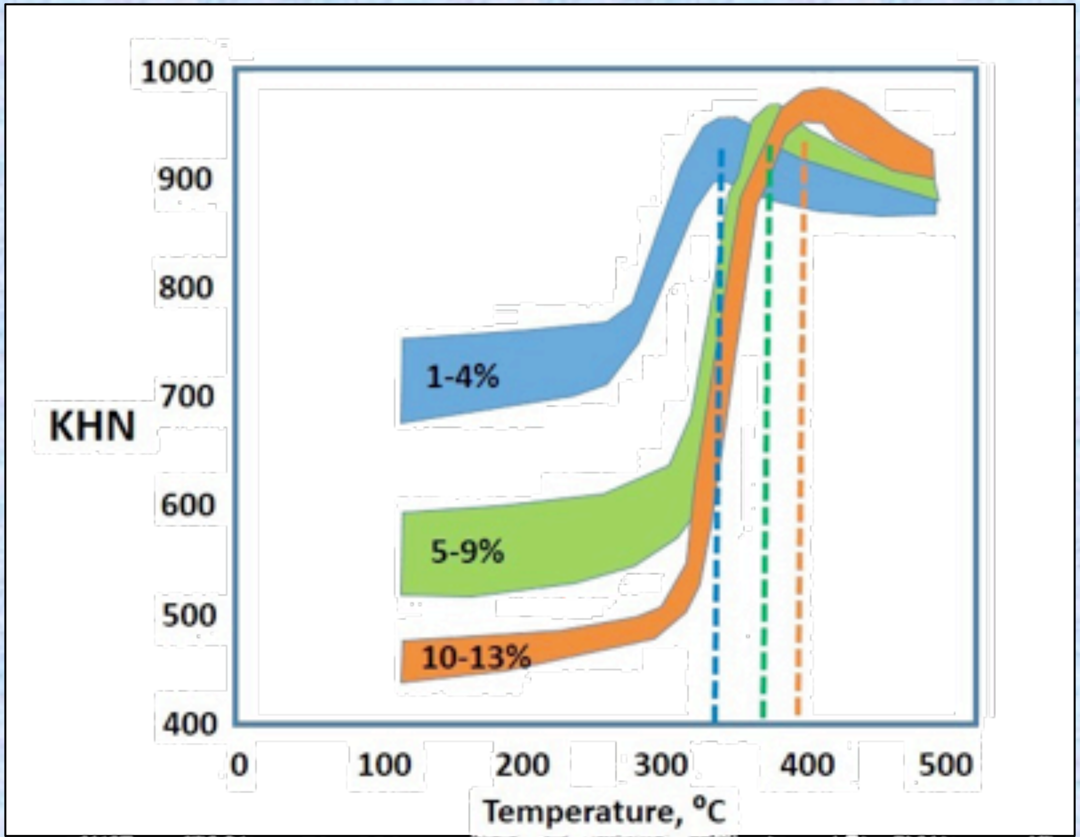


After



Heat treatment produces an intermetallic structure:
Ni_xP_y or Ni_xB_y

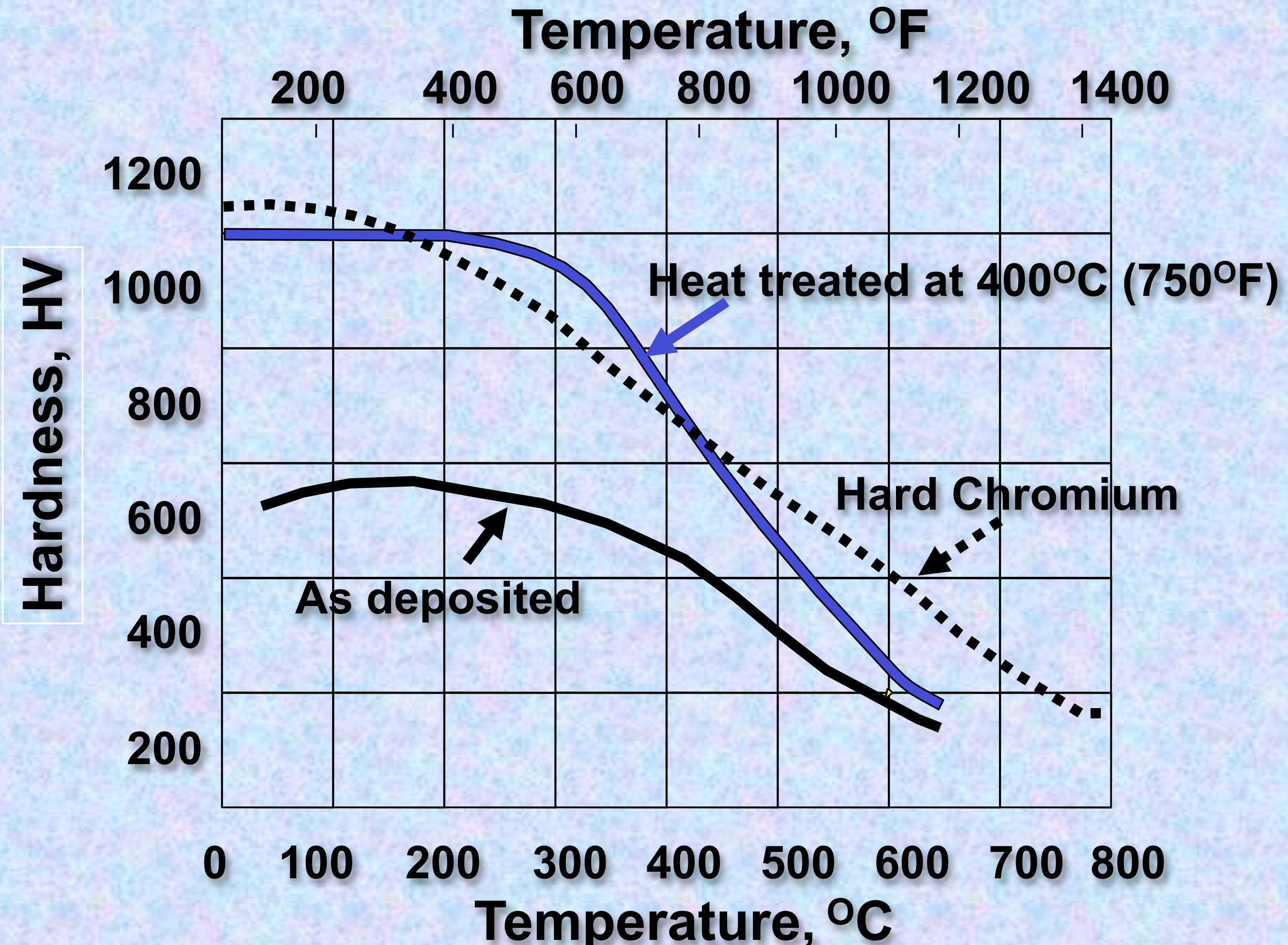
Examples:
Ni_3P, Ni_5P_2, $Ni_{12}P_5$
For Heat Treated Ni-B Alloys:
Ni_2B_3, NiB, Ni_3B_2



Effect of 1 hour heat treat on hardness for various %P EN Deposits

Source: Properties & Applications of Electroless Nickel, Nickel Development Institute

Hardness of (10%P) EN @ Elevated Service Temperatures



Abrasion Resistance

Phosphorus in EN provides lubricity, minimizes heat buildup, reduces scoring and galling

Taber Wear

Coating	Heat Treatment	Index
Watts Nickel	None	25
Electroless Ni-9%P	None	17
Electroless Ni-9%P	300°C/1 hr	10
Electroless Ni-9%P	500°C/1 hr	6
Electroless Ni-9%P	650°C/1 hr	4
Electroless Ni-5%B	None	9
Electroless Ni-5%B	400°C/1 hr	3
Hard Chromium	None	3

Falex Wear

Coating	Heat Treatment	Hardness VHN	Plated Block Wear mg	Unplated Pin Wear mg
Chromium	None	1100	0.5	1.9
EN-9%P	None	590	6.6	0.2
EN-9%P	290°C/2 hrs	880	1.2	0.1
EN-9%P	290°C/16 hrs	1050	0.4	0.1
EN-9%P	400°C/1 hr	1100	0.5	0.2
EN-9%P	540°C/1 hr	750	1.4	0.1

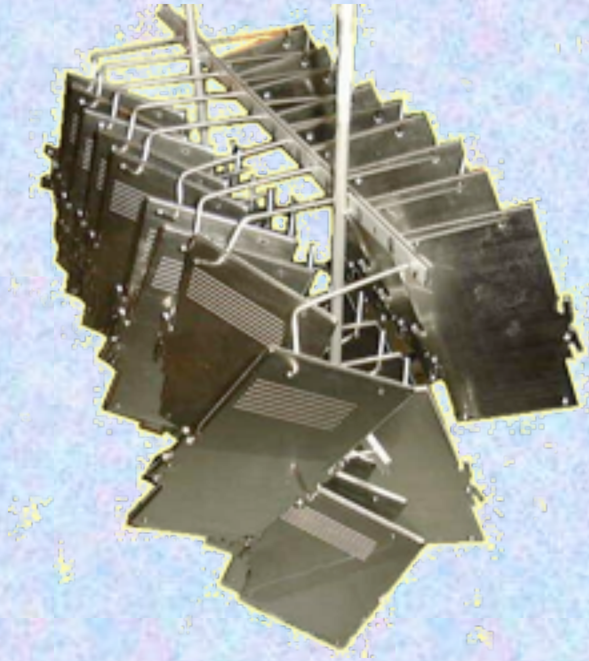
Lubrication: White Oil
Source of data: Electroless Plating; Fundamentals & Applications by Mallory and Hajdu

EN coefficient of friction (steel) = 0.13 (lubricated)
0.4 (dry) vs. Cr @ 0.14

Solderability & Weldability

Soldering Issues:

- **Low/Medium P EN is easily soldered with mildly activated rosin (RMA) flux**
- **Preheating 100-110^{O}C (210 to 230^{O}F) improves solderability**
- **Oxidized surfaces require rosin activated (RA) flux**



General Welding Issues:

- **Low welding point**
- **Phosphorus diffusion may embrittle steel.**
- **Special high purity stainless steel electrodes and inert gas shielding improves weldability**

Best consulting job in a lifetime!!!!

Hard Chromium

General Features:

- Can plate intricately shaped parts
- Low coefficient of friction
- Excellent wear at broad range of temperature
- High hardness (56-74Rc, HV900-1150)

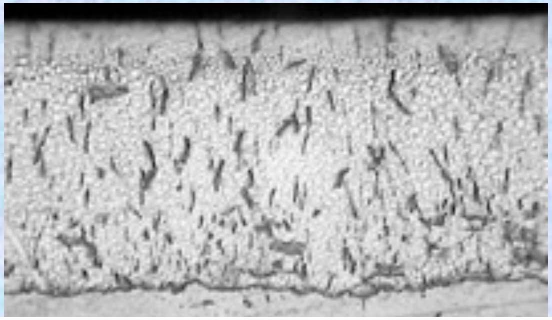
Hard Chromium on Motorcycle Drive Gear

HVOF Spray Competes with Hard Chromium

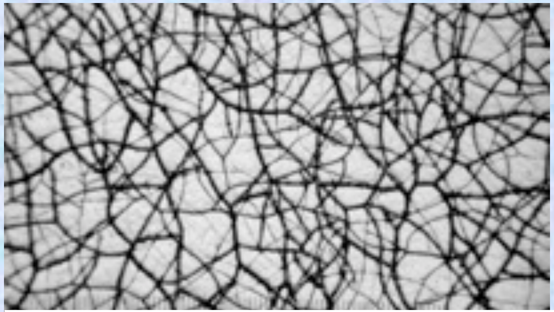
*Note: Dry lubricants cannot be used on Thin Dense

Hard Chromium-Structure

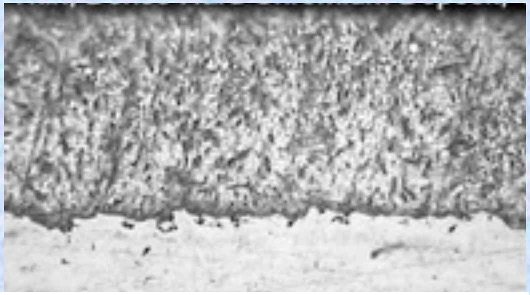
- **Deposit from the conventional solution is micro-cracked**
- **Approximately 1000 to 2,000 cracks per linear inch are produced**
- **Cracks are produced by shrinkage of deposit as chromium-hydride decomposes to chromium metal**
- **Cracks do not travel through the entire deposit**
- **“Leakage” of hydraulic fluid at high operational pressures may occur**
- **Alternate plating solutions can produce “crack-free” and “thin dense” deposits**



Cross section of conventional deposit 100X



Etched surface of conventional deposit 100X



Cross section of thin dense 100X

photos by F. Altmayer

Hard Chromium vs. HVOF

Hard Chromium Adhesion

- **Bond strength of chrome plate (on steel) = 10,000-70,000 psi**
- **Depends on preplate etching method and coating thickness*:**

Etch chemistry	Plating Current density A/dm^2	Shear strength*, kg/cm^2 Coating thickness, microns 60	150	350
CrO_3 200g/l, H_2SO_4 2g/l 54°C	35	5400	3300	
	50	4200	2600	1800
H_2SO_4 53°Bé (66%w/w) Room temperature	35	7000	4100	
	50		3400	2000

*Average of two measurements. Plating conditions: CrO_3 250g/l, H_2SO_4 2.5g/l, 54°C.

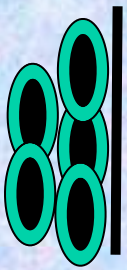
Data Source: E. Zmihorski, *J. Electrodepositors' Tech. Soc.*, 23, 203 (1947-48)

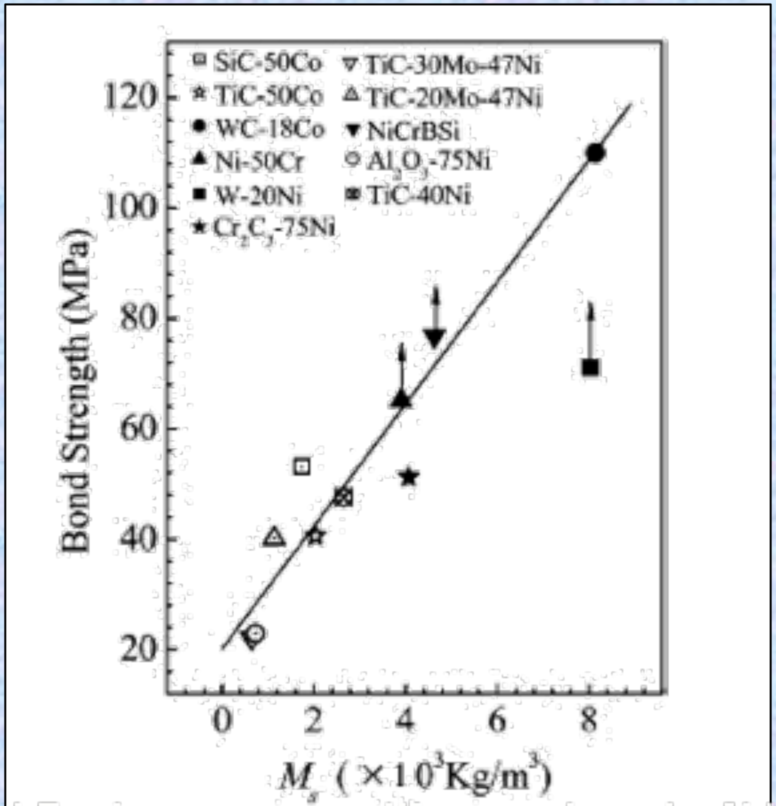
Hard Chromium vs. HVOF

HVOF Spray Adhesion:

- **Bond strength of HVOF coatings = 17,000 psi**
- **Depends on mass of solid phase in powder**

- For Wear:
--Fe-Cr-Mo
--Fe-Ni-Cr-Mo
- For Corrosion Resistance:
--Ni-Cr-W-Mo





Powder impact speed ~800m/s

Data Source: Y.-Y. Wang et al. / Surface & Coatings Technology 200 (2006) 2923–2928

Hard Chromium vs. HVOF

Corrosion Resistance:

Hard Chrome:

- **Good salt spray resistance**
  - **Depends on thickness, RMS finish of base metal/ final deposit**
- **Poor crevice corrosion resistance**
  - **Especially in chloride environments**

HVOF Coatings:

- **Good salt spray resistance**
- **Excellent crevice corrosion resistance**

Hydraulic shaft plated with 0.0004” hard chromium after 6 hours of salt spray exposure

MD-80 Slat Track
HVOF sprayed on wear surfaces

Hard Chromium vs HVOF

Hardness-Chromium:

- Optimized at ~50°C, 45A/dm^2
  - Typically HV700-1100 (56-74Rc)
  - Thin, dense deposits are 5-10% harder
  - Chromium softens at high service temperatures
  - BCC structure at >HV1000, hexagonal at <HV700

Hardness-HVOF:

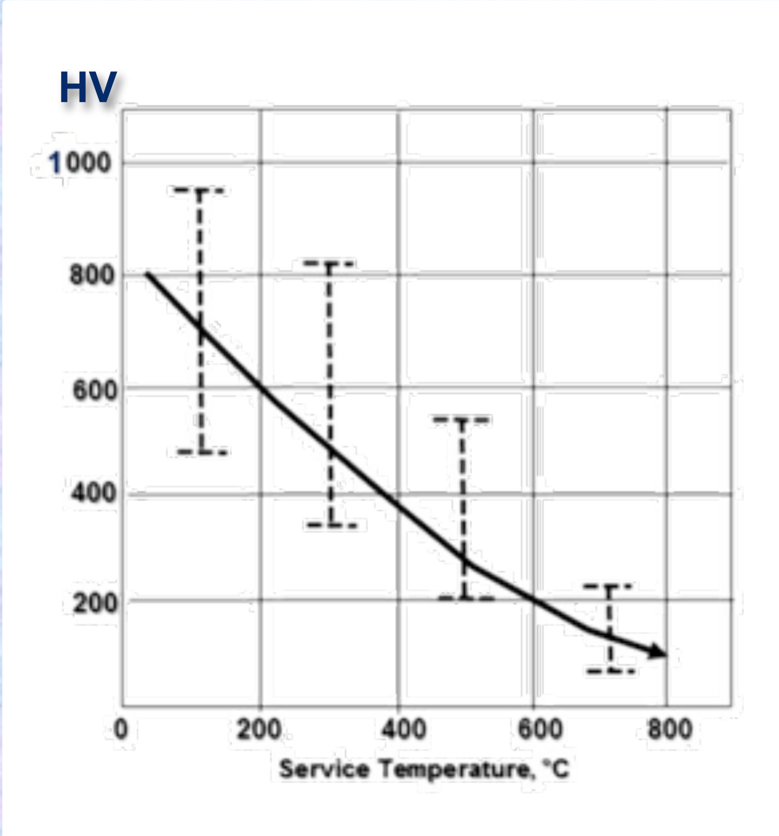
- HV1150-1350 (>75Rc)

Wear-Chromium:

- Hardness-wear may not be related
- Taber Index = 0.04 (10,000 cycle test)

Wear-HVOF

4 to 5 X hard chromium



Hardness of hard chromium vs. service temperature

Hard Chromium vs, HVOF

Internal Stress-Hard Chromium:

- **Is a function of plating thickness and plating solution temperature**
- **Is typically tensile [as high as +110kg/ mm^2 (157ksi)] reducing fatigue strength**
  - **Shot peening can help**

Internal Stress-HVOF:

- **Stress is compressive**

Coefficient of Friction-Hard Chromium:

0.1-0.2 depending on base metal

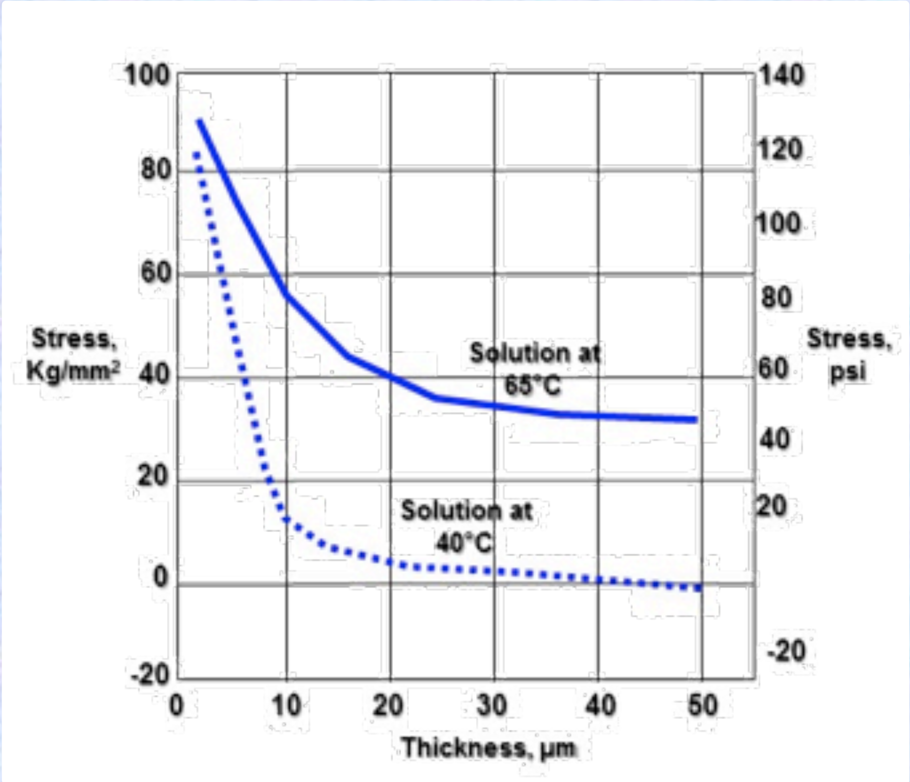
Electrical Resistivity:

~60 µohm-cm

- **lower if plated at higher temperature (>60°C)**

Melting Point:

1890-1920°C



Internal Stress-Hard Chromium

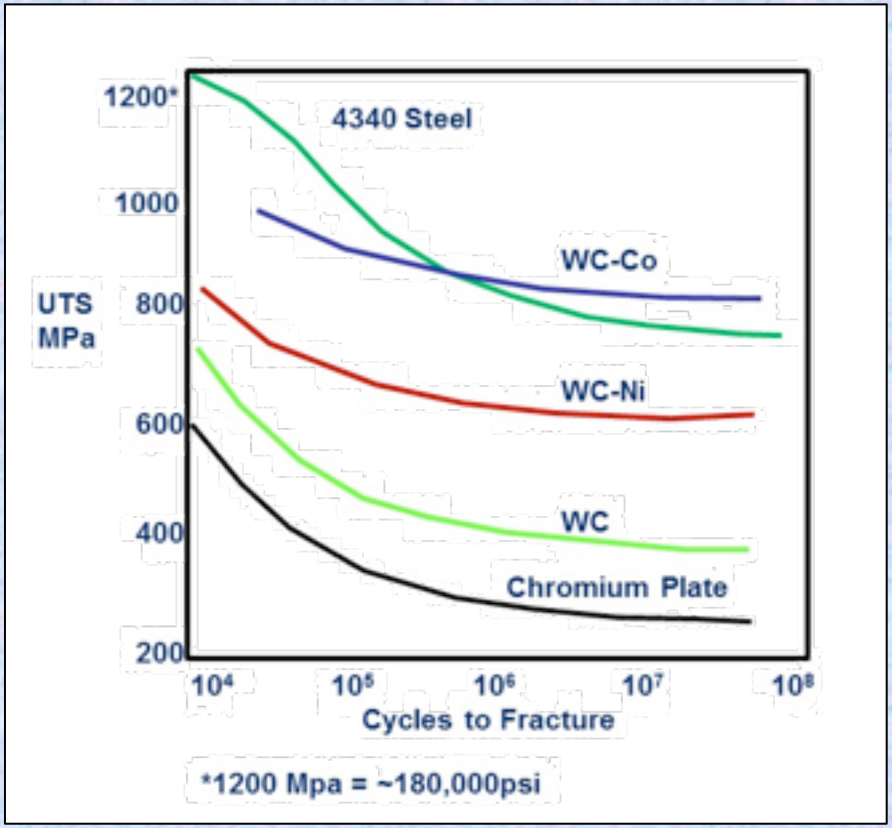
Hard Chromium vs. HVOF

Impact on Fatigue- Hard Chromium:
- Lowers fatigue strength of steel

Impact on Fatigue- HVOF:
- Lower Fatigue Strength but to a lesser degree than chrome
- At elevated cycles some coatings enhance fatigue strength

Tensile Strength/Ductility-Hard Chromium
- Typical tensile strengths = 10-13 kg/mm^2 (15-19ksi)
  - Higher TS can be obtained at higher than normal temperatures and current density
- Ductility = 0 (<0.1% elongation)

Tensile Strength/Ductility-HVOF:
- No data



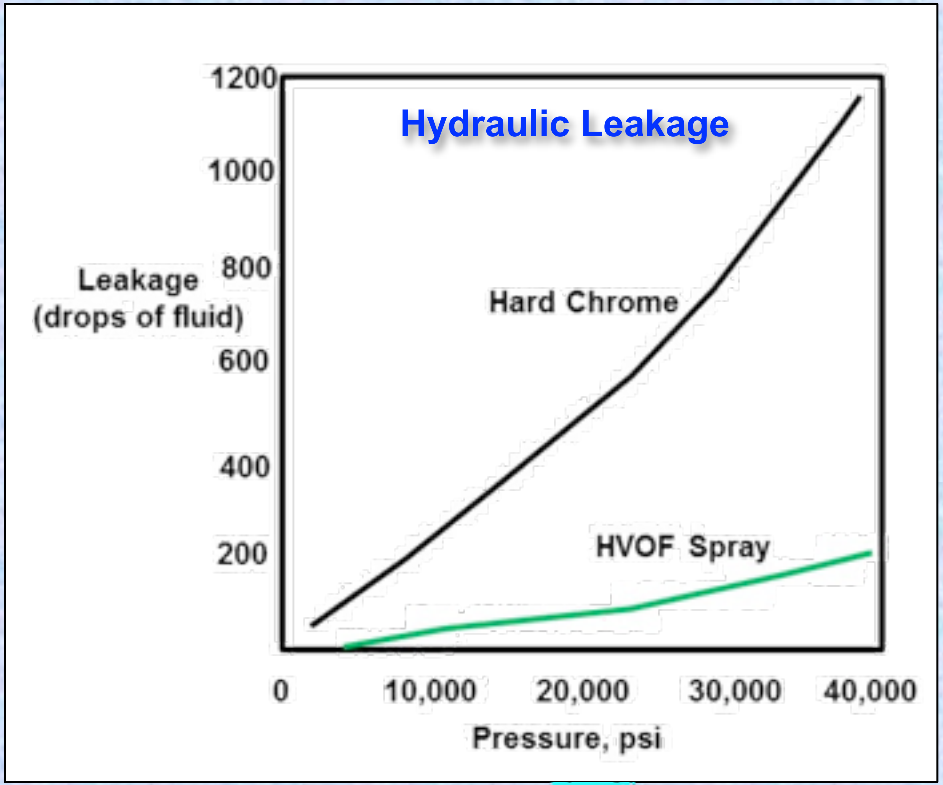
Hard Chromium vs. HVOF

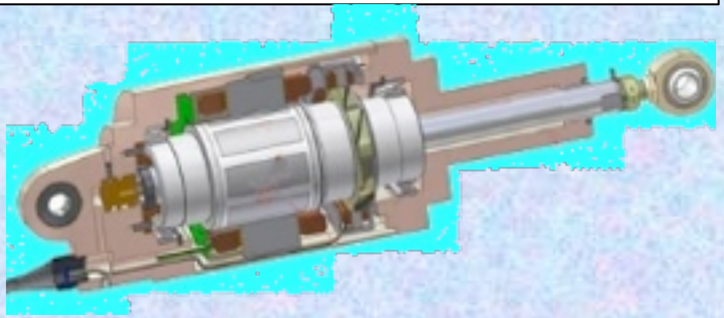
Hydraulic Leakage:

• **Higher than HVOF spray**

Hydraulic Leakage Cures:

- **Thin dense over “regular” hard chrome**
- **Vacuum impregnation**





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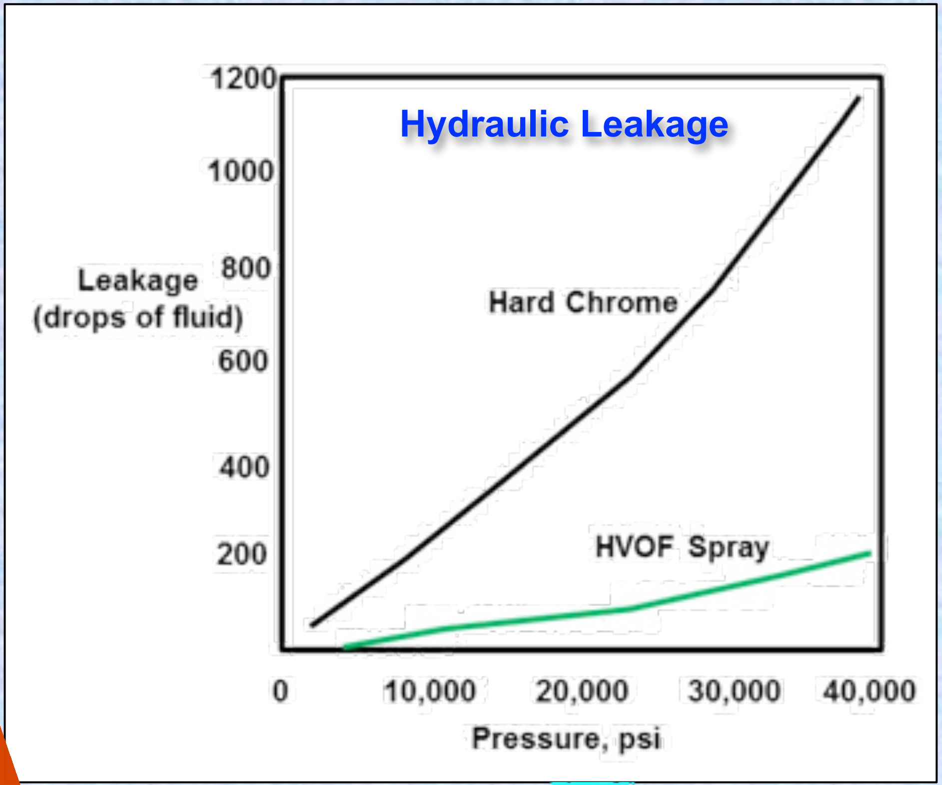

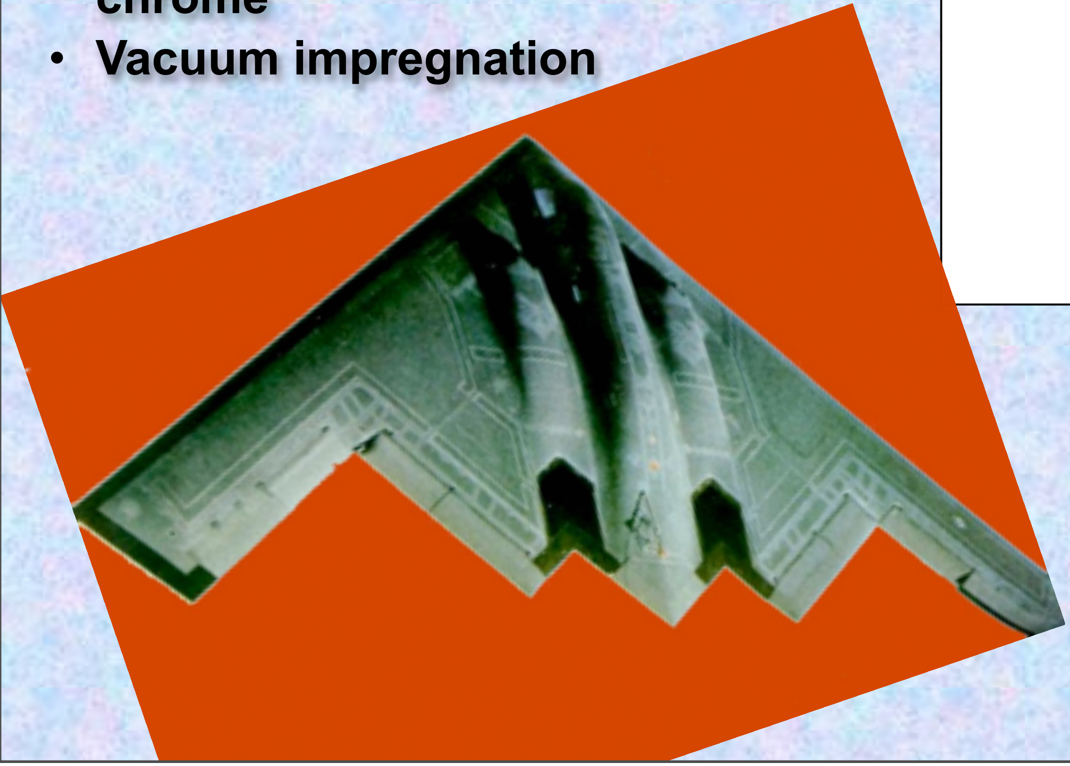

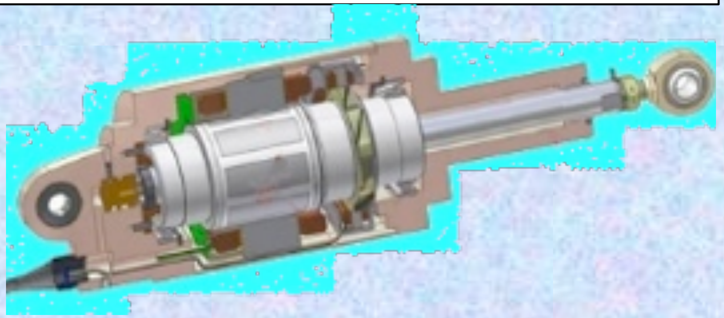

The End, Thank You!