SilcoTek® Technology

Designing Surfaces for Performance

ASM International
South Central Pennsylvania Chapter
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SilcoTek Corporation

Outline

- SilcoTek Introduction
- Basic Process
- Applications / Industries
- SilcoNert 2000
- Dursan
- Research

SilcoTek Corporation

- Started as Restek division in 1996 (RPC)
  - Proposal by 4 employees
- Independent Company in 2009
  - 14 employees
- 38,000 sq. ft. facility in August 2013
  - Currently 45 employees

SilcoTek Driving Innovation

SilcoTek Corporation

- What we do
  - Surface design and modification
  - Take substrate performance beyond original design and capabilities
  - ***<u>Gain control of the surface</u>***

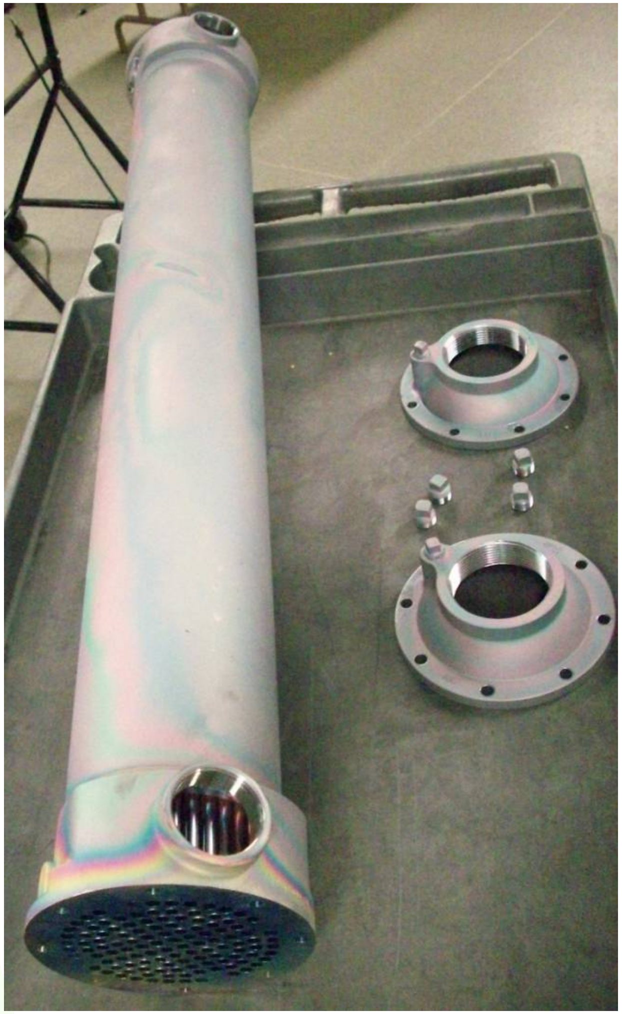
- How do we do it?
  - Chemical vapor deposition
  - Surface functionalization

General Process Characteristics

- Non line-of-site
- Thermal only (400-450°C) – no plasma, etc.
- 3-dimensional – everywhere / all surfaces
- Uniform coating (relative)
- Bulk processing
  - 42,000+ parts February
- Multiple substrate types
  - Metallic, ceramic, glass
- Long tubing coils

General Process Limitations

- Substrate composition: thermal limits
  - Plastics, etc.
  - Aluminum
- Substrate composition: deposition limits
  - Copper, magnesium, nickel, gold, silver
- Size
  - Largest cylindrical vessel: 64” h x 30” ID



Coating Process

1. Receive customer-supplied items
   – Inspect, photograph and alert of any discrepancies

2. Surface preparation
   – Standard: caustic, aqueous, ultrasonic baths
   – Custom: solvents; removal of fluorinated grease; etc.

Coating Process

3. Chemical vapor deposition (CVD)
   - Vacuum
   - Temperature (up to 450°C)
   - Pressure
   - Gas precursors

Coating Process

4. Post-clean (CO_2, aqueous sonication)
5. Quality inspection & digital documentation
6. Safe packaging and shipping

Coating: First Impressions

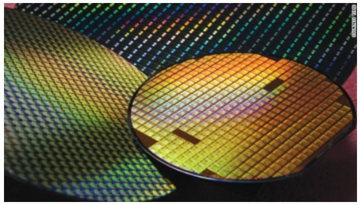
- Color – indicative of thickness
  - 100-1500nm
  - Color changes with ±50 Å
  - Colors will cycle with thickness

Surface Solutions

General Inertness	Corrosion prevention
Moisture barrier	Hydrophobicity
Sulfur Inertness	Coking/fouling prevention
Mercury Inertness	Low surface energy, easy-cleaning
Ammonia Inertness	Ultra-high vacuum enabler
Prevent Protein Sticking	

Industries Served

- Chromatography, Analytical Chemistry
- Refining and Petrochemical
- Semiconductor Manufacturing
- Bio/Pharma
- Automotive and Aerospace
- Chemical Manufacturing
- Oil and Gas Exploration and Transport



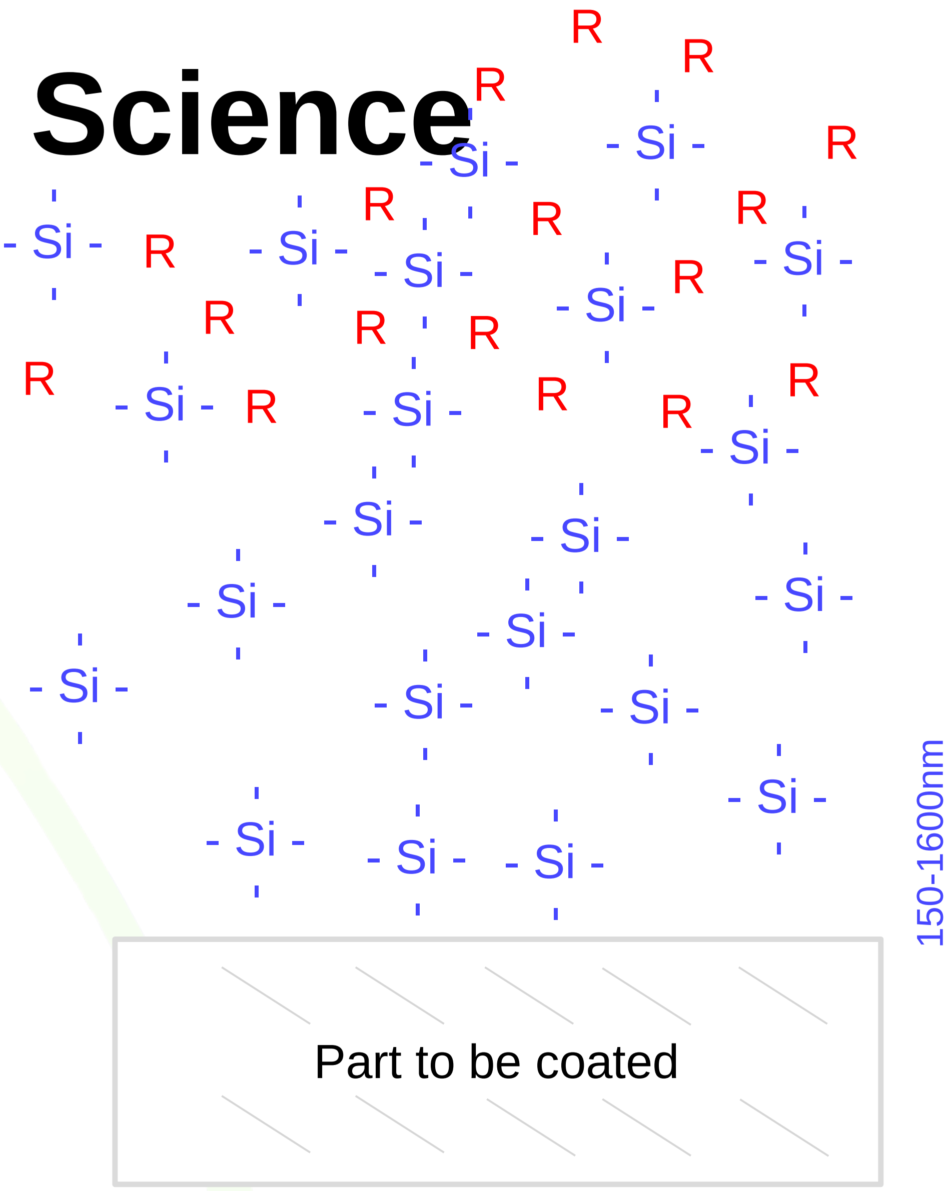
SilcoTek®
Driving Innovation

Coating Science

- Coatings consist of a Base Layer and a Surface Functionalization

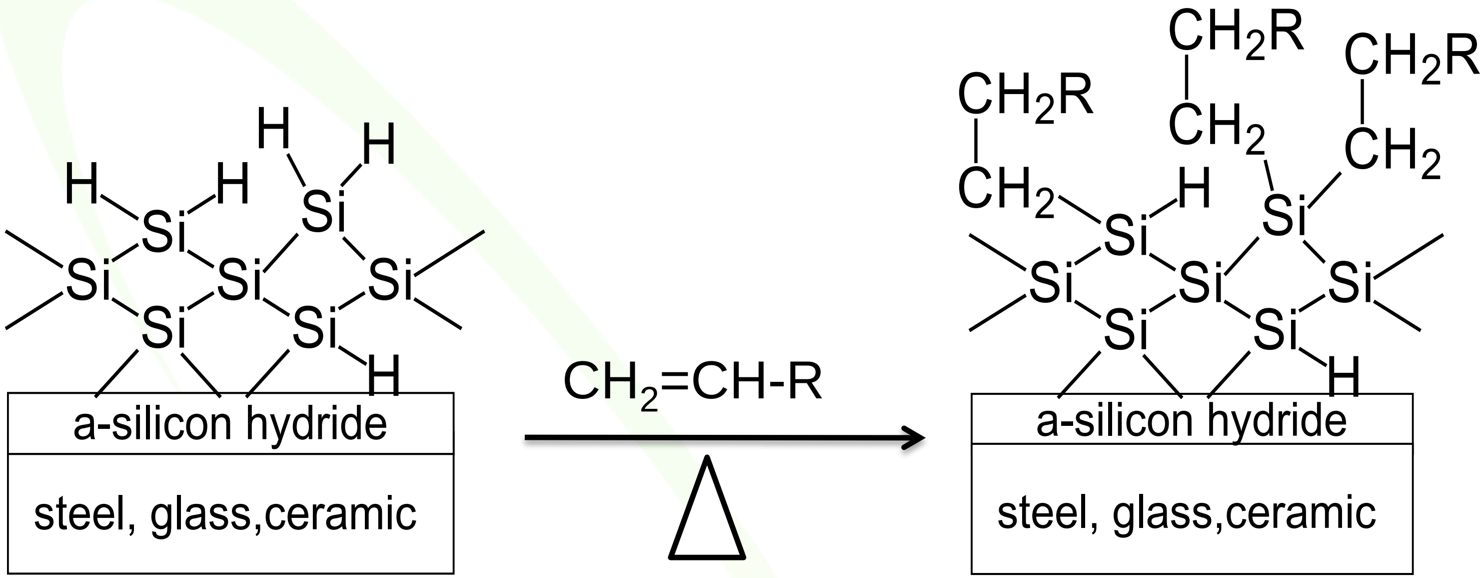
  – Base is 150-1600nm of:
    - Si (Silco) or
    - Si – C – O (Dur)

  – Functionalized surface – Chemistry is key to performance



SilcoTek
Driving Innovation

SilcoNert 2000 – circa 1995



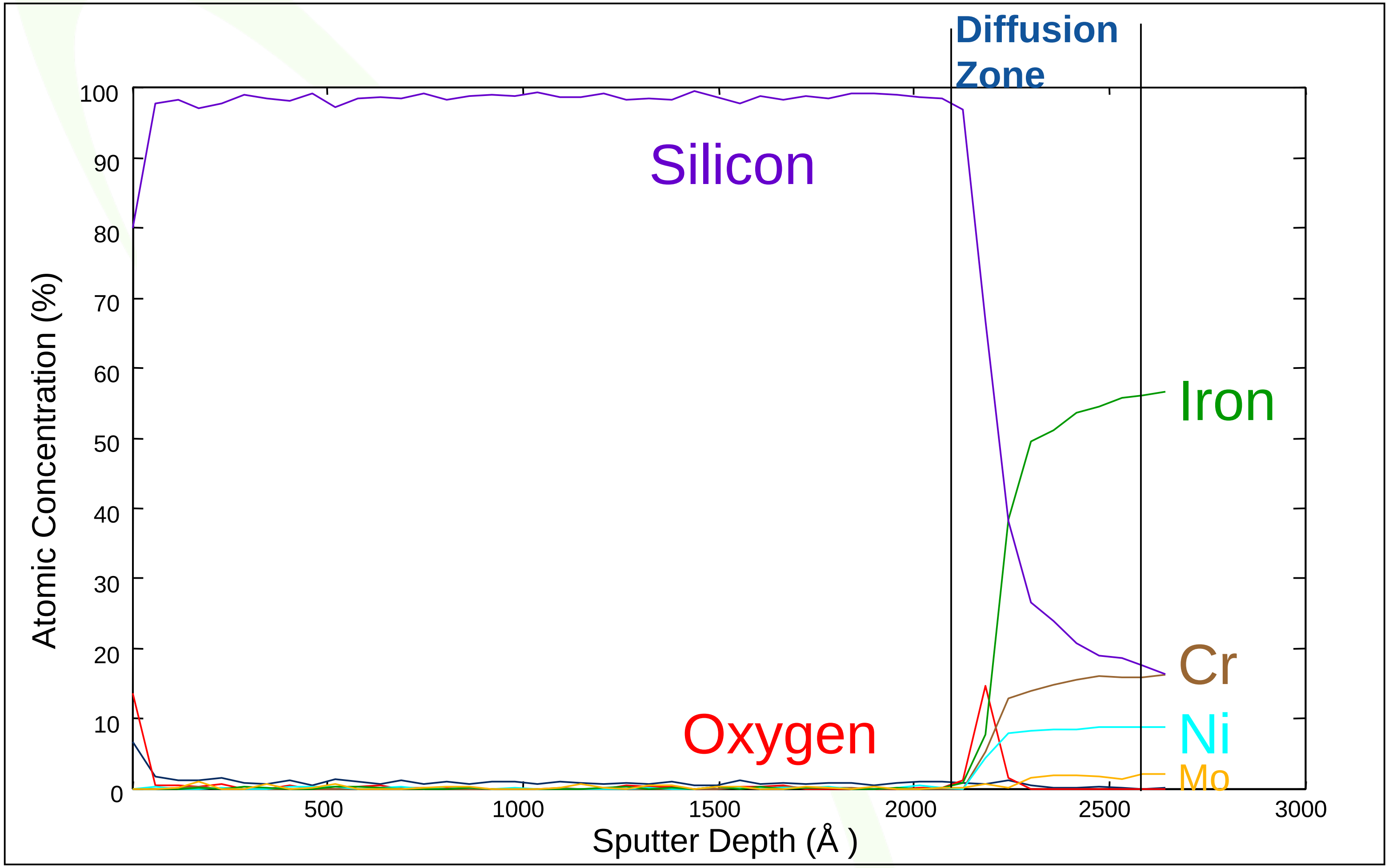
(SN1000) (SN2000)

- Hydrosilylation via ß-hydride addition

$$\equiv Si\text{-}H + CH_2{=}CH\text{-}R \longrightarrow \equiv Si\text{-}CH_2\text{-}C(H)(H)\text{-}R$$

US Pat. #6,444,326; 7,867,627

Auger Depth Profile: SilcoNert 2000



In-House Characterization

- FT-IR
  - Transmission
  - Specular Apertured Grazing Angle
  - Attenuated Total Reflectance
- Contact Angle
  - Goniometer / Tensiometer
- Thickness
  - Filmetrics F20 and F40
- Electrochemical Impedance Spectroscopy

Partnership with Penn State

Millennium Science Complex: State of the Art Analytics

SilcoTek R&D at PSU: Trained users

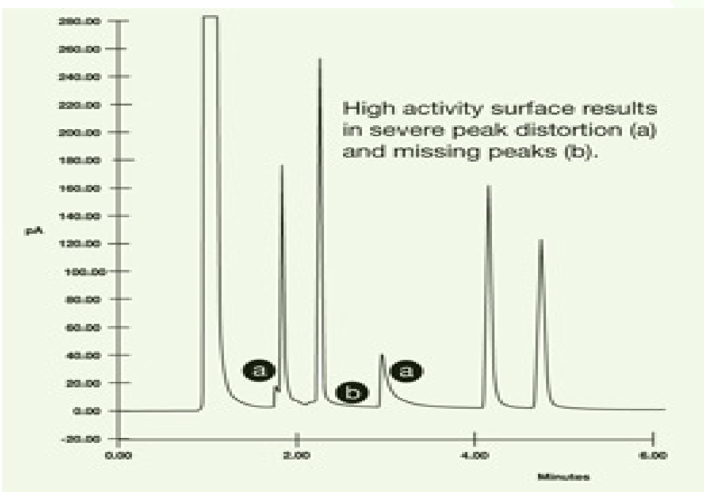
- Electron Microscopy (SEM, ESEM, FESEM, EDX)
- Focused Ion Beam (FIB) / SEM
- X-ray Photoelectron Spectroscopy (XPS)
- Auger Electron Spectroscopy (AES)
- Raman Microscope Spectroscopy
- FT-IR Microscope Spectroscopy
- Optical Profilometry
- Atomic Force Microscopy (AFM)

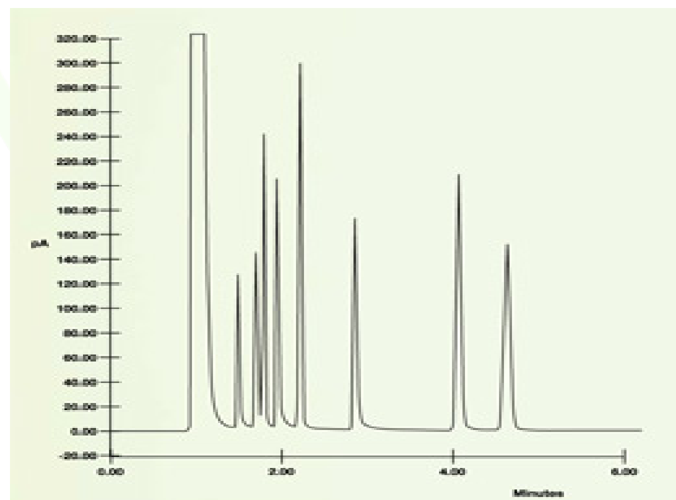
Access to:

- Time of Flight Secondary Ion Mass Spectroscopy (TOF/SIMS)
- Tribological Measurements
- Electrochemical Measurements
- Scanning Tunneling Electron Microscopy (STEM)

SilcoNert 2000 creates a chemically inert flow path

- First major successful application (~1996): GC columns and accessories.
  - Accurate analytical profile of all trace compounds
  - Eliminate false negatives
  - Get a reliable sample from field to lab
  - Used in manufacturing process systems and analytical laboratories



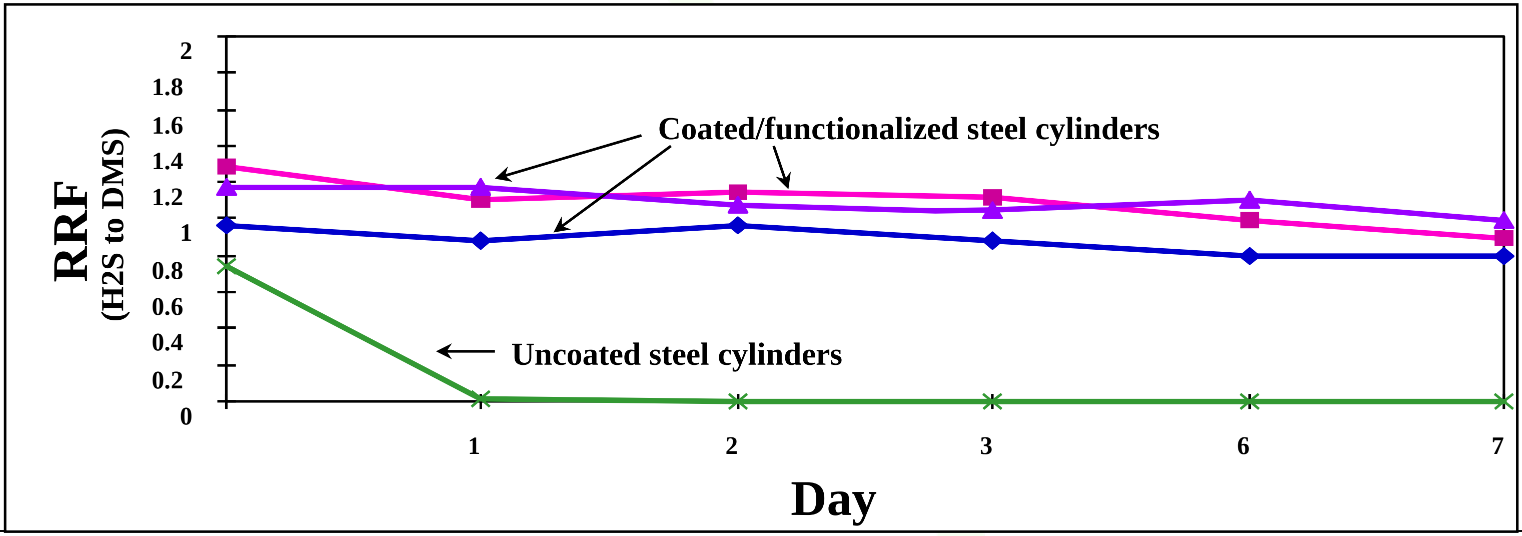


SilcoNert 2000 Chemical Inertness

- Stainless steel hides trace compounds:
  - Adsorbs sulfurs: methylmercaptan, H_2S
    - “Total Sulfurs”
  - Causes loss of ammonia and mercury
  - Holds on to polar organics e.g. alcohols
- In 1990’s new low sulfur regulations pushed need to analyze wells, refinery processes, emissions
- SN2000 enabled existing systems to meet new regulations

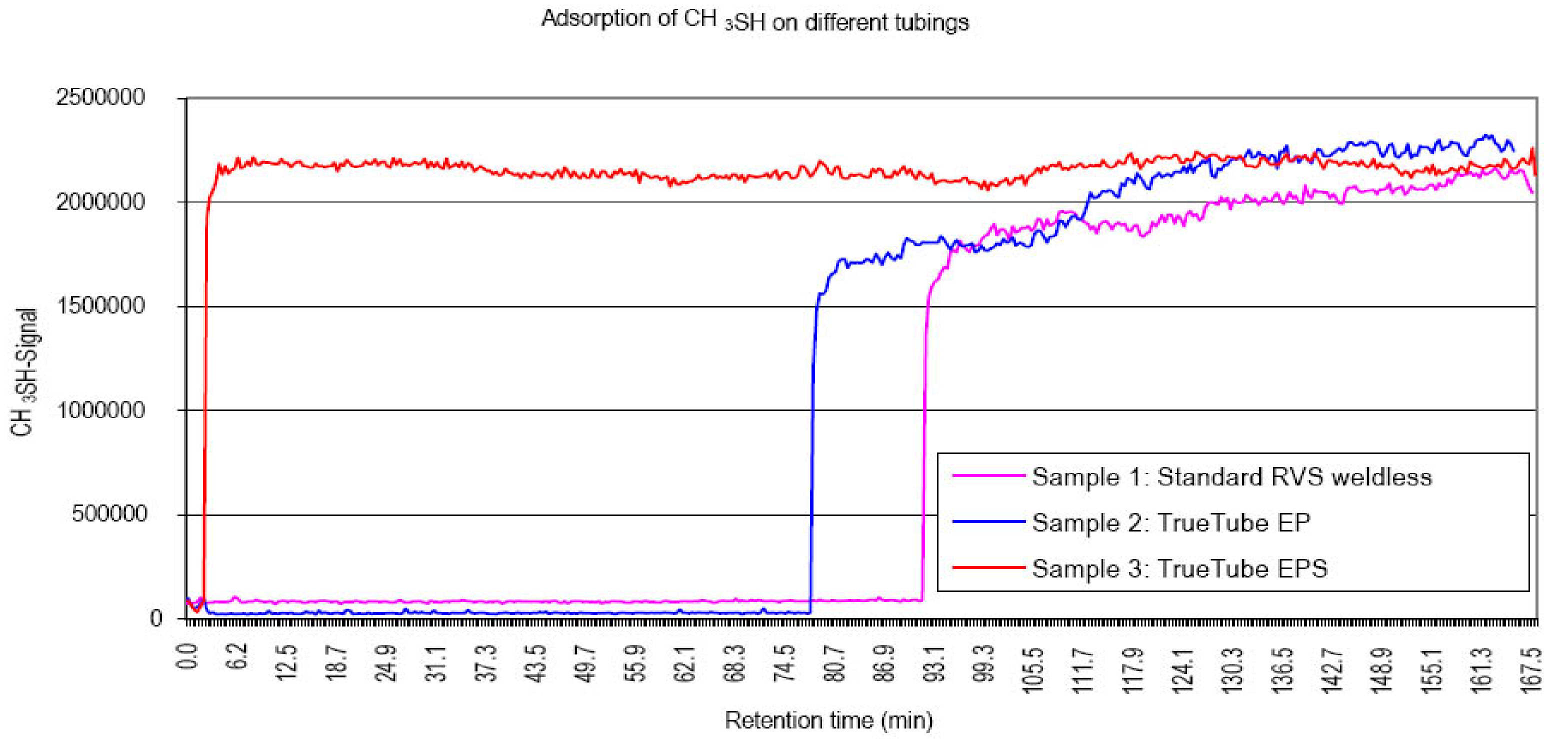
SN2000 Coated vs. Uncoated

- 500ml 304SS sample cylinders (and valves)
- 10ppb H_2S holding study over 7 days



SilcoNert 2000 Improves Transfer

Reduce sample adsorption by 98%
Improve Process Response
Improve Yield



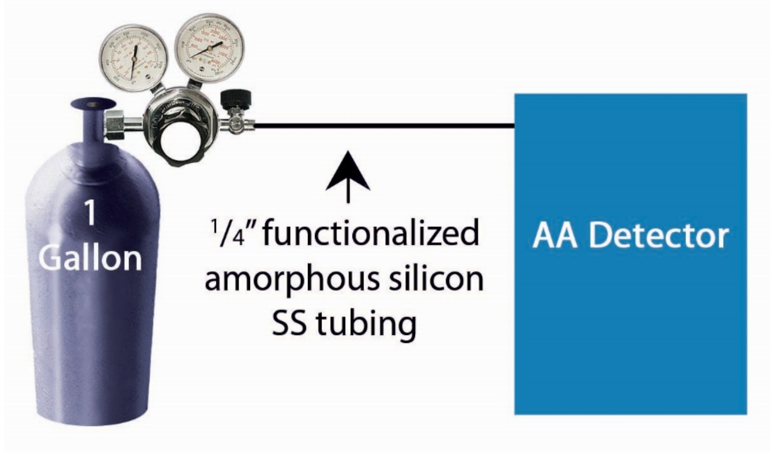
- 100’ x 1/8” tubing
- 0.5ppm mercaptan

Mercury on SN2000

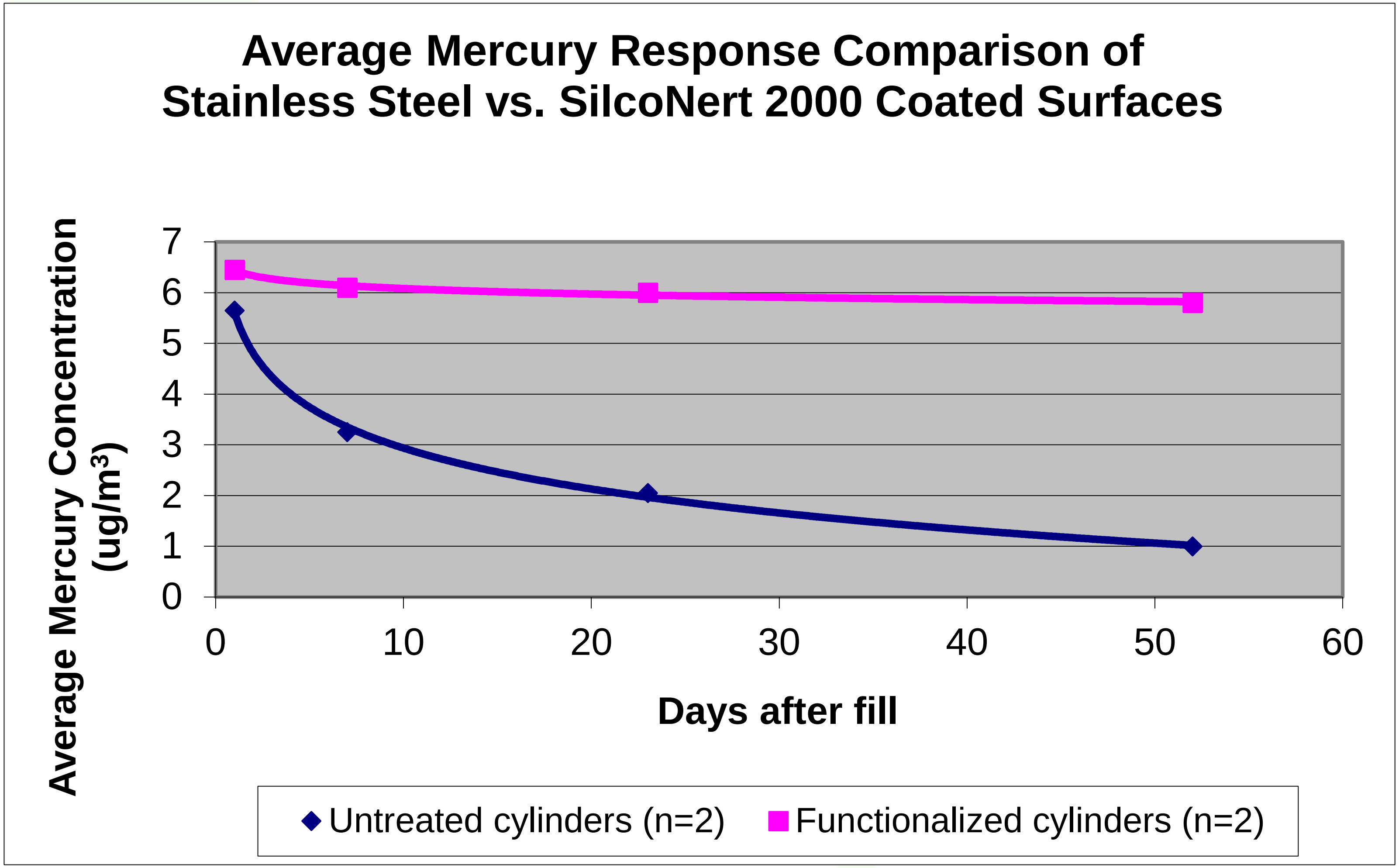
- Mercury in oil and gas wells is common in many different geographical areas.
- Must be monitored to prevent damage to pump vanes and pipelines
- Dangerous if not measured accurately; like sulfurs, Hg adsorbs onto wetted flow paths
- Impossible to analyze without SilcoNert coated pathways

Low-level Hg Comparative Analysis

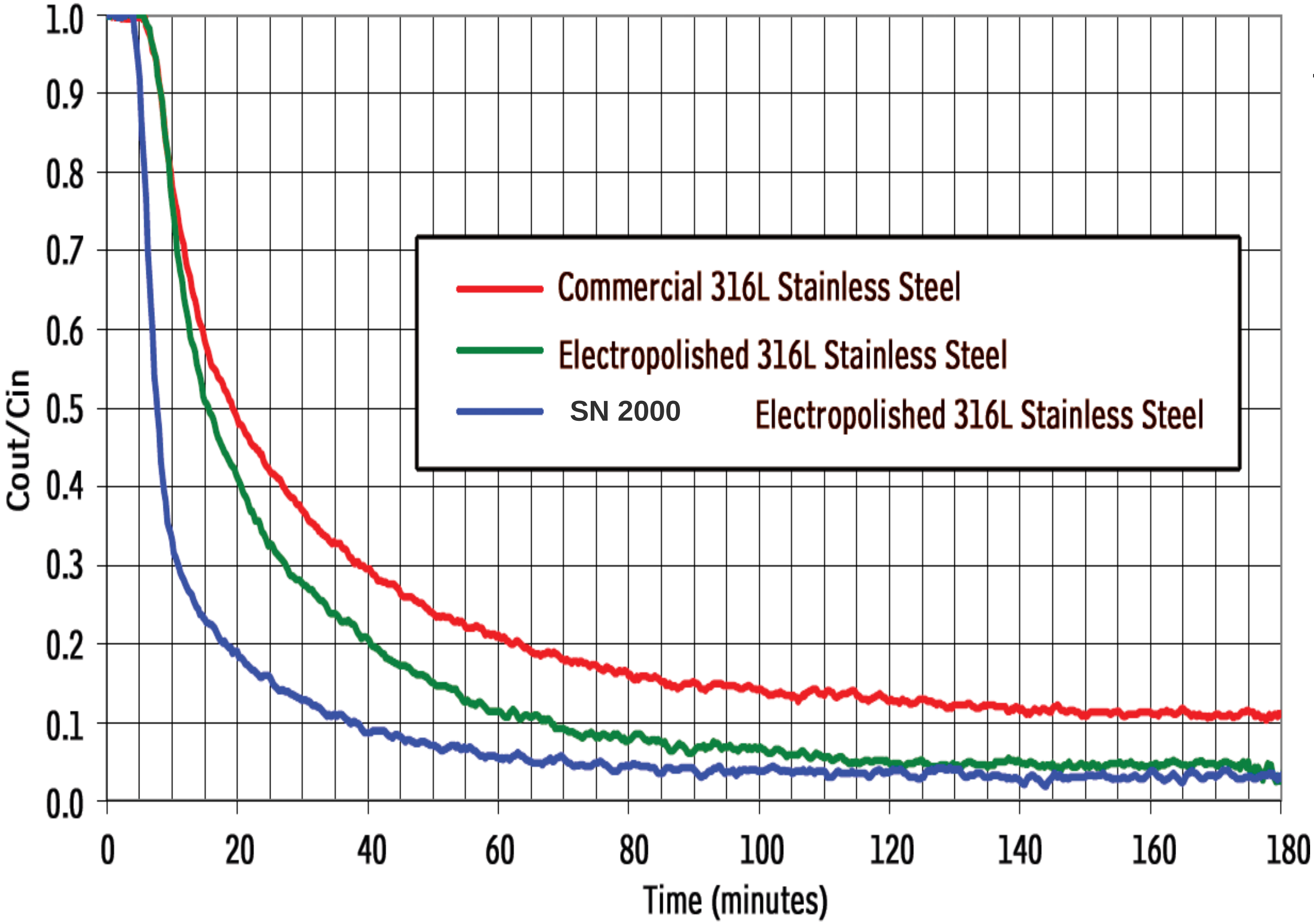
- 5 µg/m³ Hg Standard (5 ppt)
- 1 Gallon Sample Cylinder 1800psi DOT rated
- Nominal Temp. 70°F
- Test Cycle Day 0,7,19,50
- Direct Interface Gas Sampling
- Atomic Adsorption Detector
- SilcoNert-treated Regulator and Tubing



SN2000 Stability



Applications Data: Drydown



Conditions:

100', ¼" tubing,

0.35 slpm, 22C

1ppm to 96% Drydown Equilibration Time:

- Commercial seamless: 180 min.
- E-polished seamless: 60 min.
- SN2000, e-polished seamless: 30 min.

Data courtesy of O'Brien Corporation, St. Louis, MO

1987-Current

- SilcoNert 1000 – Amorphous silicon
  - Barrier, inertness
- SilcoNert 2000 – Functionalized amorphous silicon
  - Best inertness
- Silcolloy – Multilayered amorphous silicon
  - Corrosion resistance
- SilcoGuard – Thinner Silcolloy
  - UHV applications
- SilcoKlean – Functionalized amorphous silicon
  - Anti-coking

Dursan®

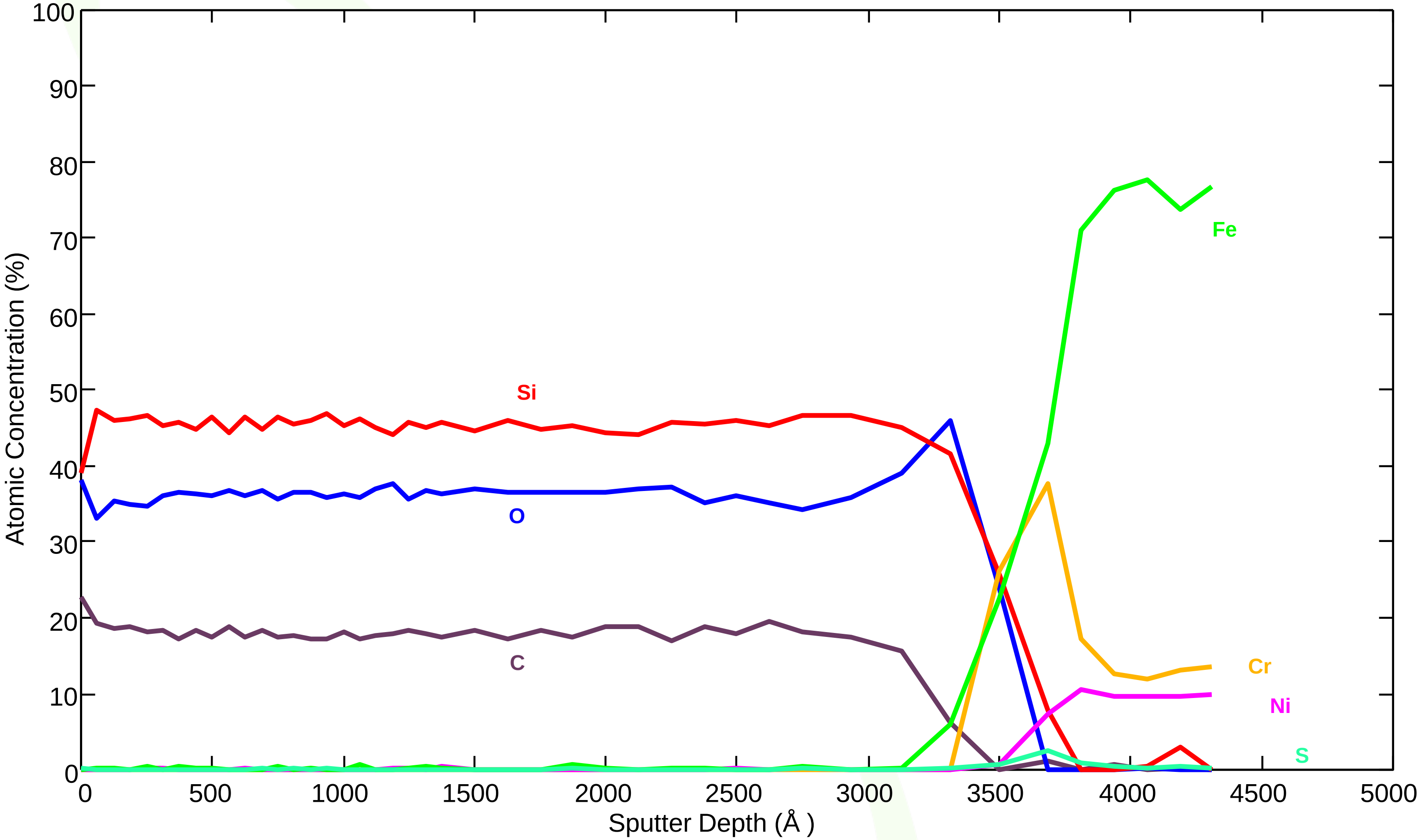
- Non-pyrophoric starting materials
- Developed to withstand rigors of down-hole oil and gas sampling
- Protection through the full pH range 0-14
- Tough + inert surface suitable for more robust analytical applications:
  - HPLC, refining, clinical diagnostics, etc.
  - Approaching inertness of SN2000
- Exceptional corrosion resistance properties
- Next Generation Coating

Dursan Deposition - 2010

- Initial deposition
  - Alkylsilane thermal decomposition
  - 450°C
- Oxidation
- Surface functionalization
  - Alkyl surface

SilcoTek® Driving Innovation

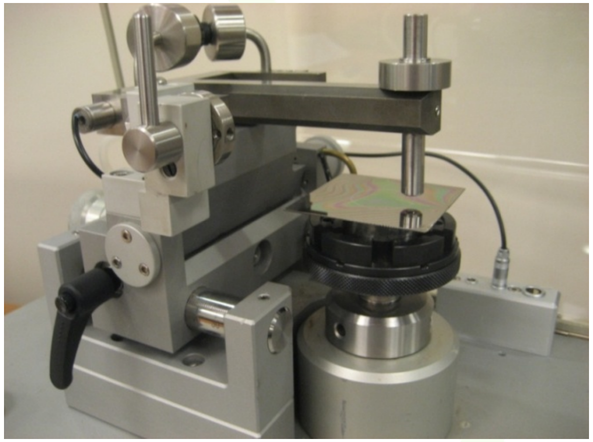
Auger Depth Profile: Dursan



Wear Resistance

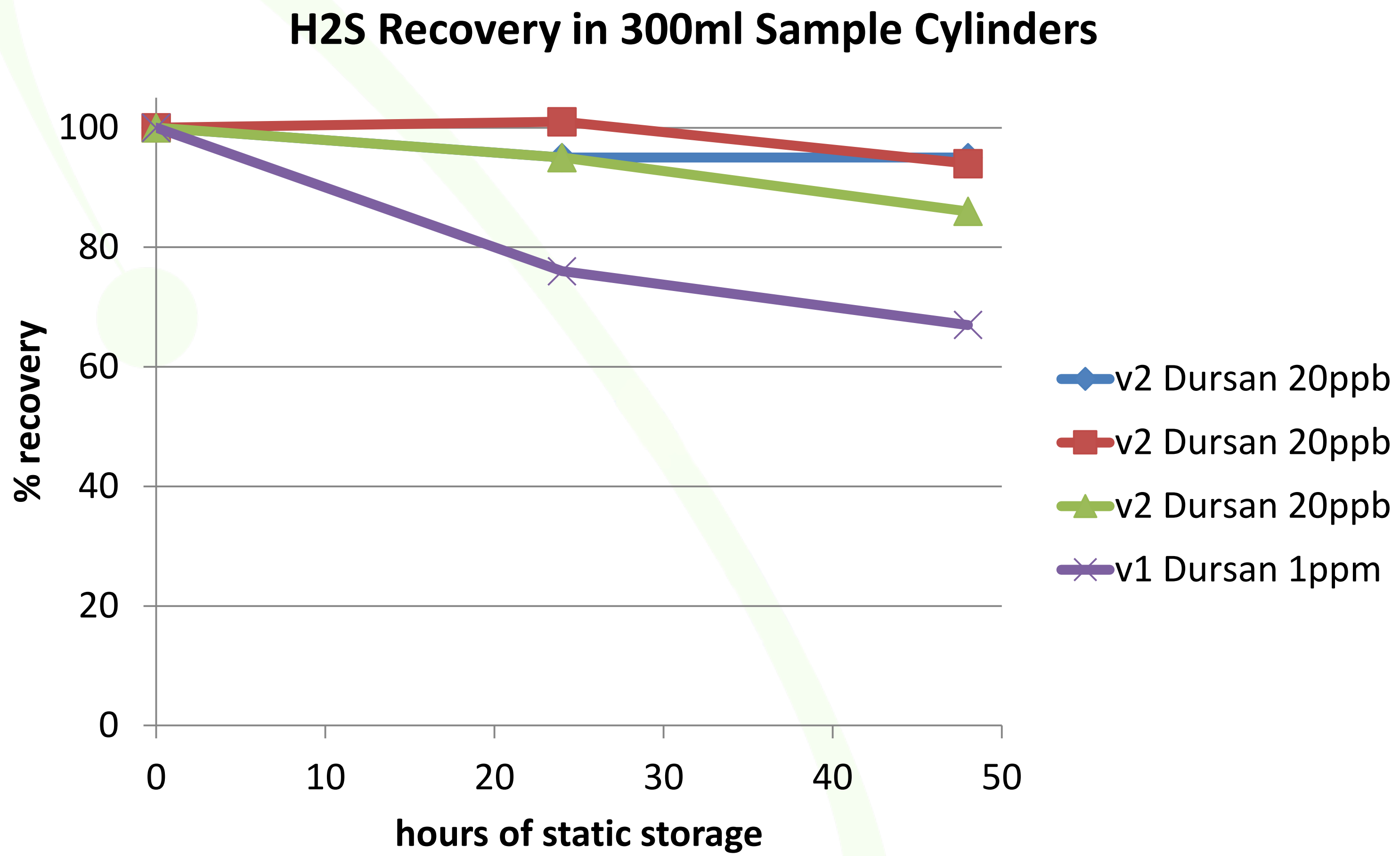
	Avg. Coeff. Friction	Wear Rate ($x10^{-5}mm^3/Nm$)
Uncoated SS	0.589	13.810
Dursan	0.378	6.129
Silcolloy	0.7	14.00

- ASTM G133 on 316 SS mirror finish



Load	2.0 N
Duration	20 min
Speed	80 rpm
Radius	3mm
Revolutions	1,554
Ball Diameter	6mm
Ball Material	SS 440

Low ppb recovery rivaling SN2000 Inertness



SilcoTek Corrosion Solutions

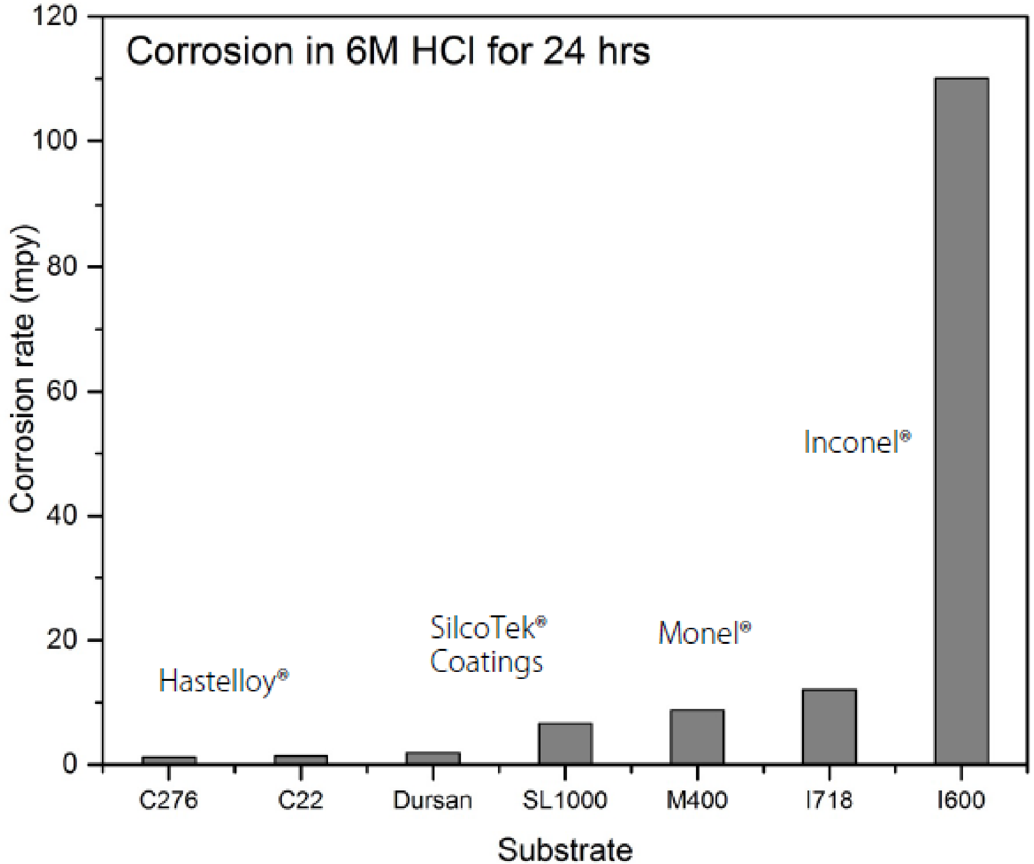
Silcolloy®

- Amorphous silicon
- Up to 0.8µm thick
- Ideal for corrosion control in high purity applications (semiconductor manufacturing)

Dursan®

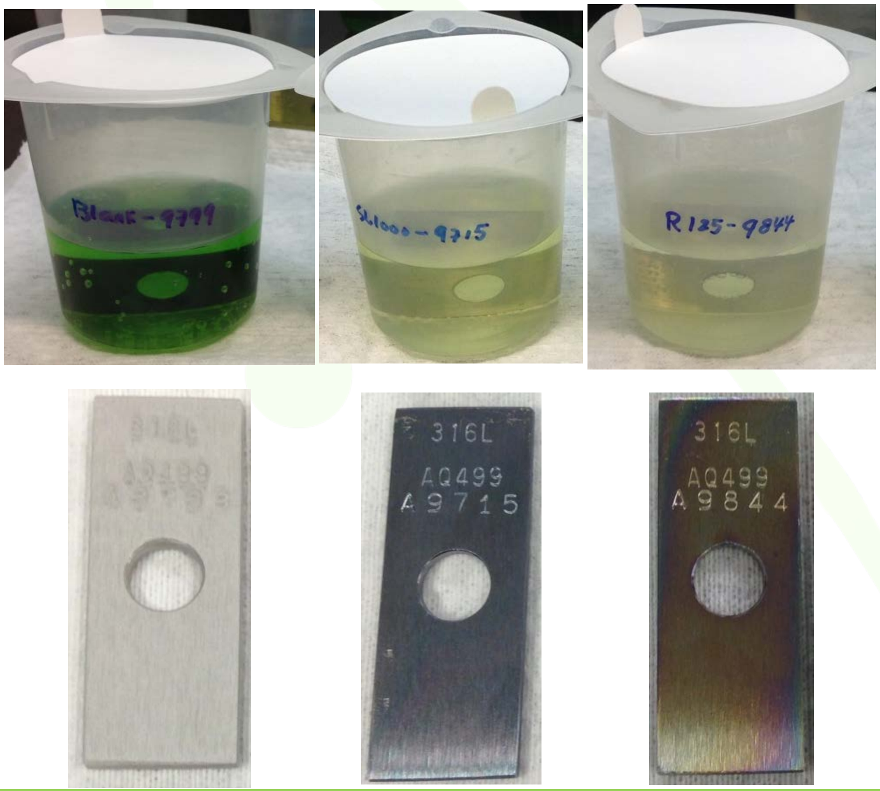
- Silicon, oxygen, and carbon
- Up to 1.5µm thick
- Ideal for pH > 7 where wear is a concern
- Newest coating

Coatings vs. High Performance Alloys

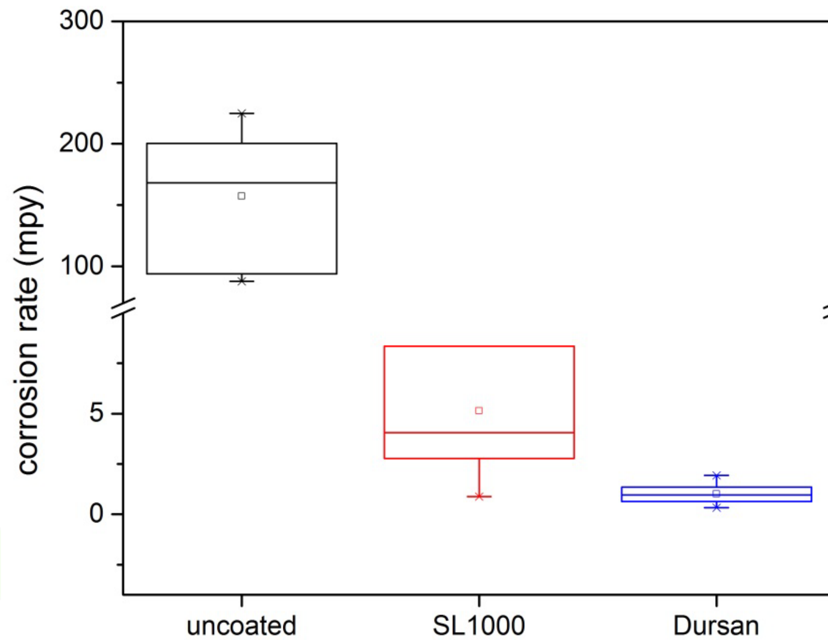


ASTM G31 Guidelines

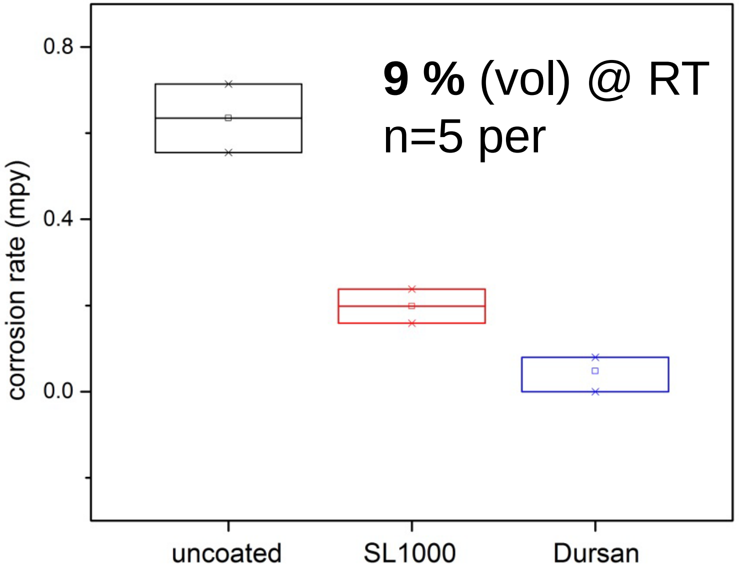
6M HCl Corrosion Resistance, 24hr @ RT

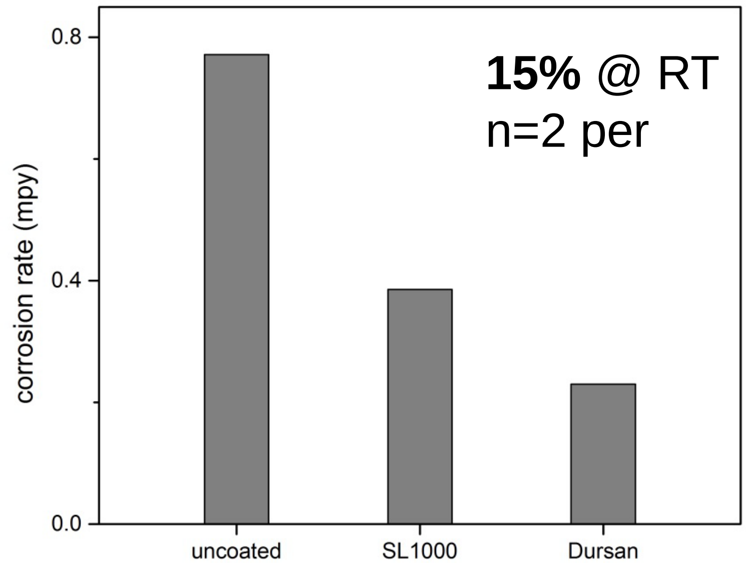


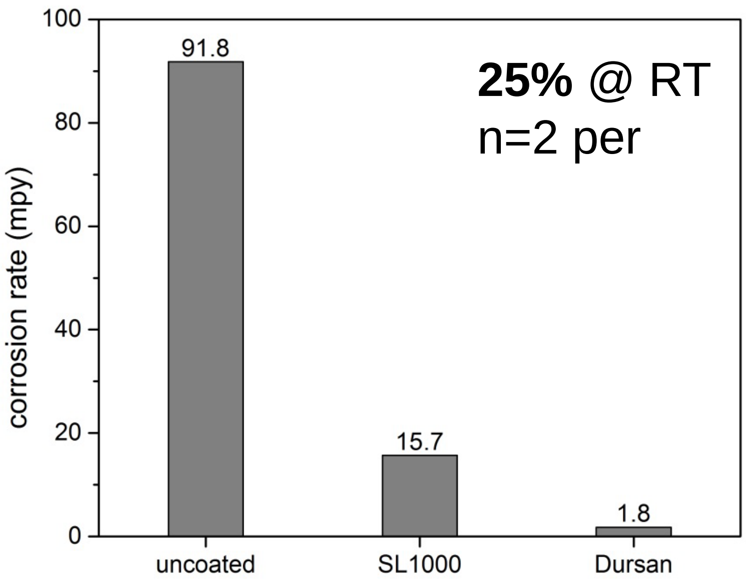
uncoated | SL1000-coated | Dursan-coated

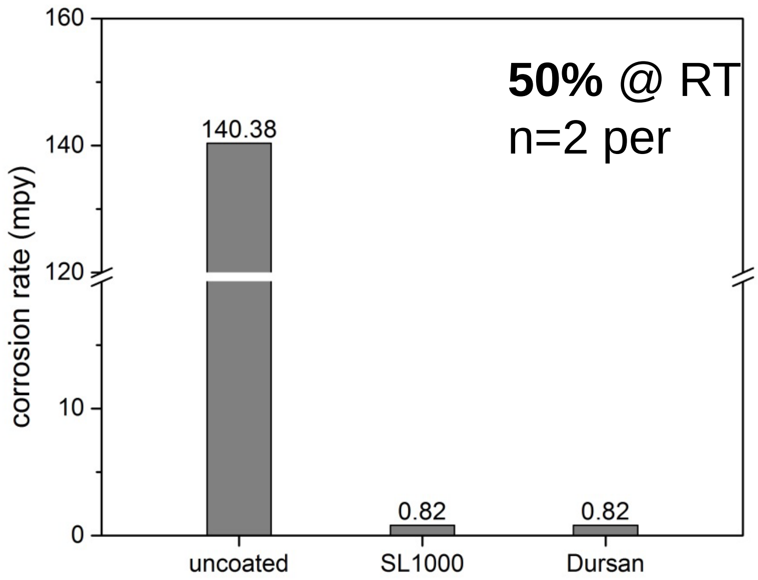


Sulfuric Acid Corrosion Resistance; 24hr

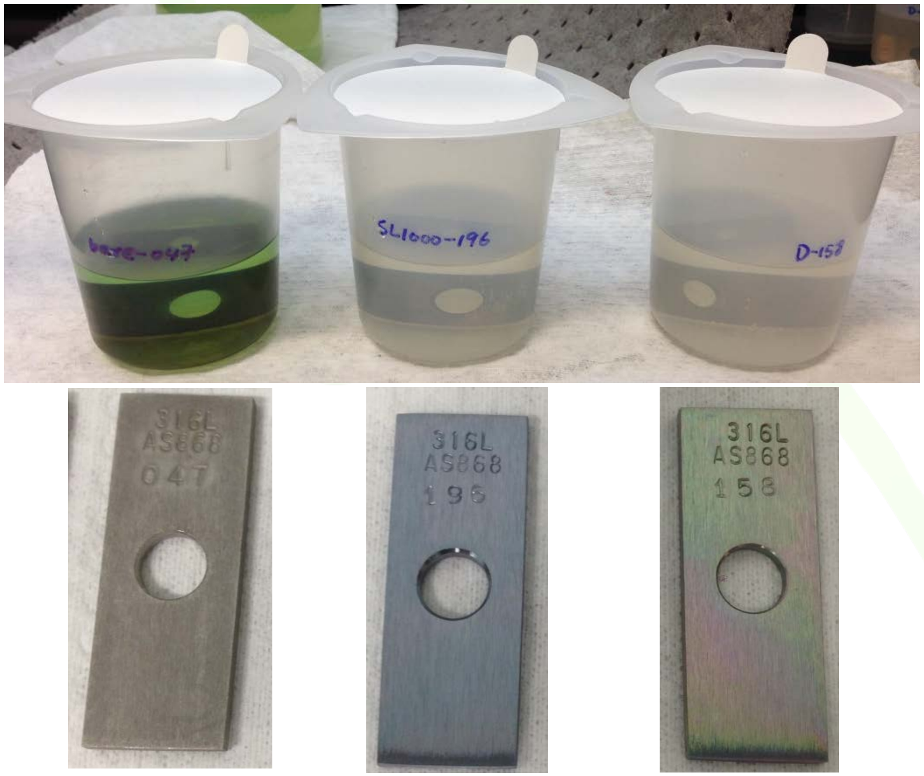




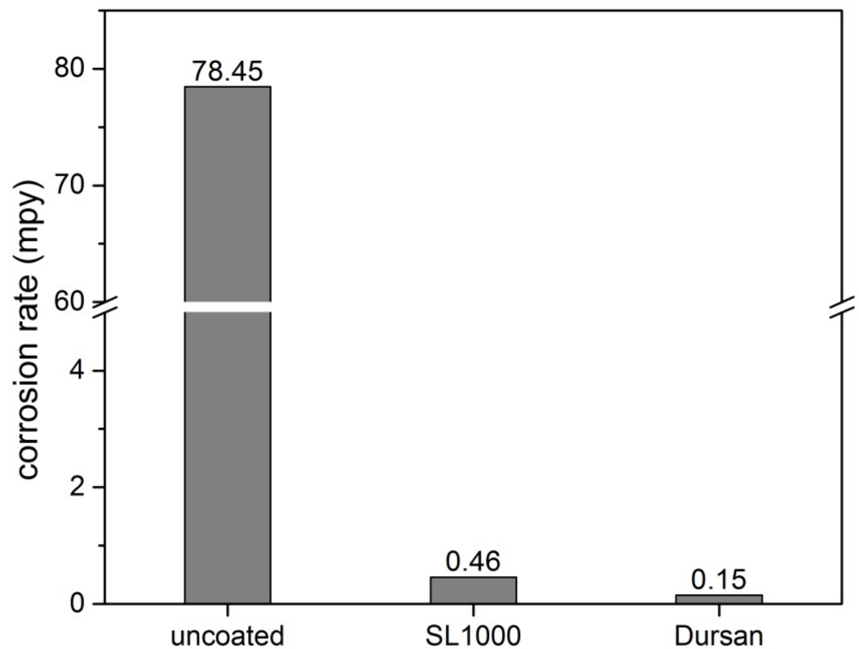




Sulfuric Acid (cont.); 85%, RT, 24hr



uncoated | SL1000-coated | Dursan-coated

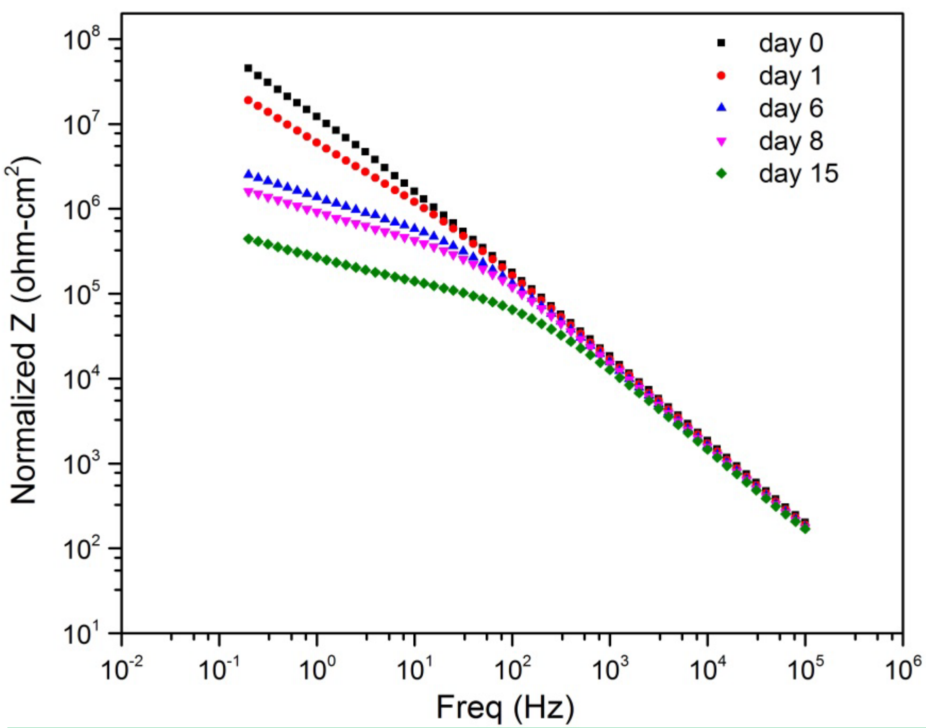


SilcoTek® Driving Innovation

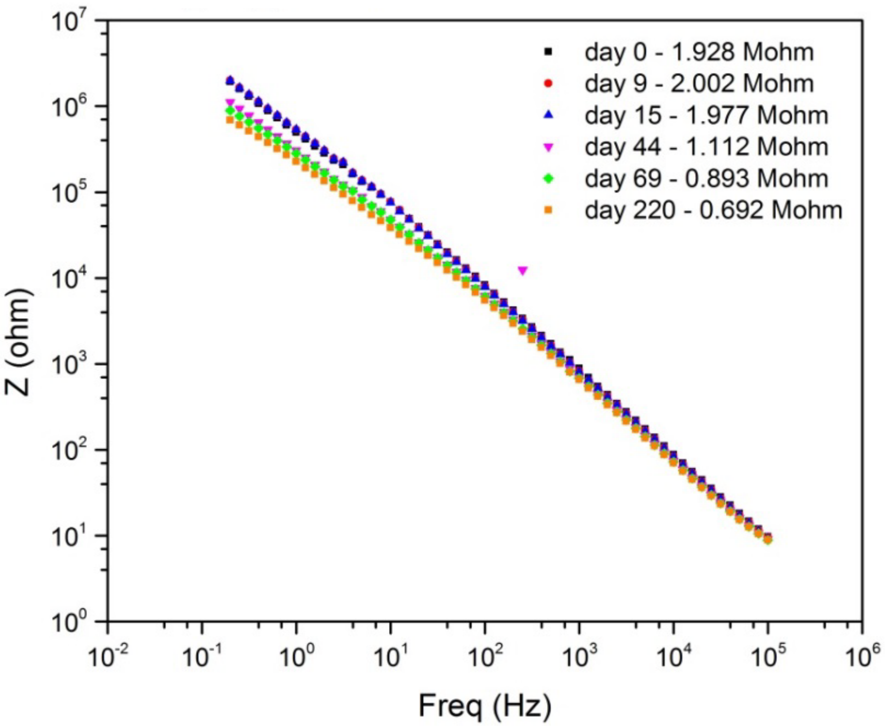
Corrosion performance comparison: EIS

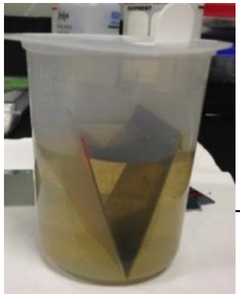
- v1 vs. v2 Dursan in 5% NaCl monitored with EIS

Original Dursan (v1)



SOP Dursan (v2)

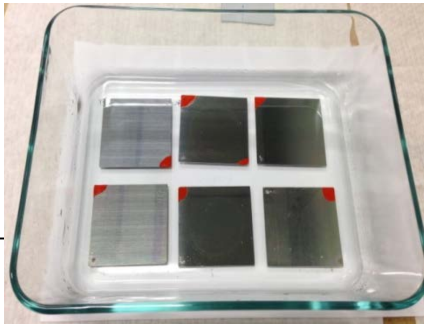




Orig. Dursan 20 days in salt water

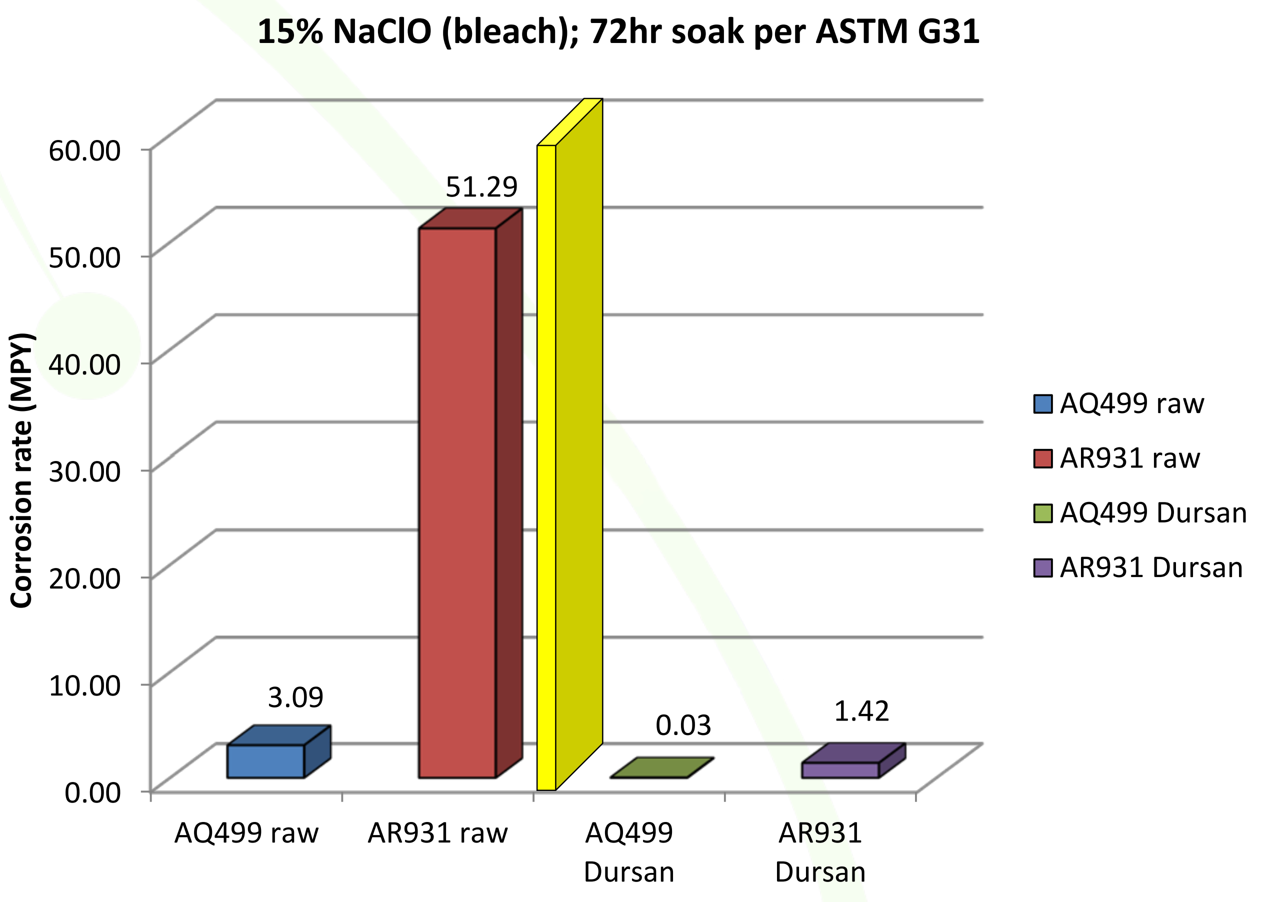
Cyclic Acidified Salt Fog Exposure:

- Currently at 4000+ hr. exposure for ASTM G85-11.A2 for Dursan
- No loss / rust



SOP Dursan 420 days in salt water

Leveling the Playing Field: "316L"



Low Surface Energy: Powerful Potential

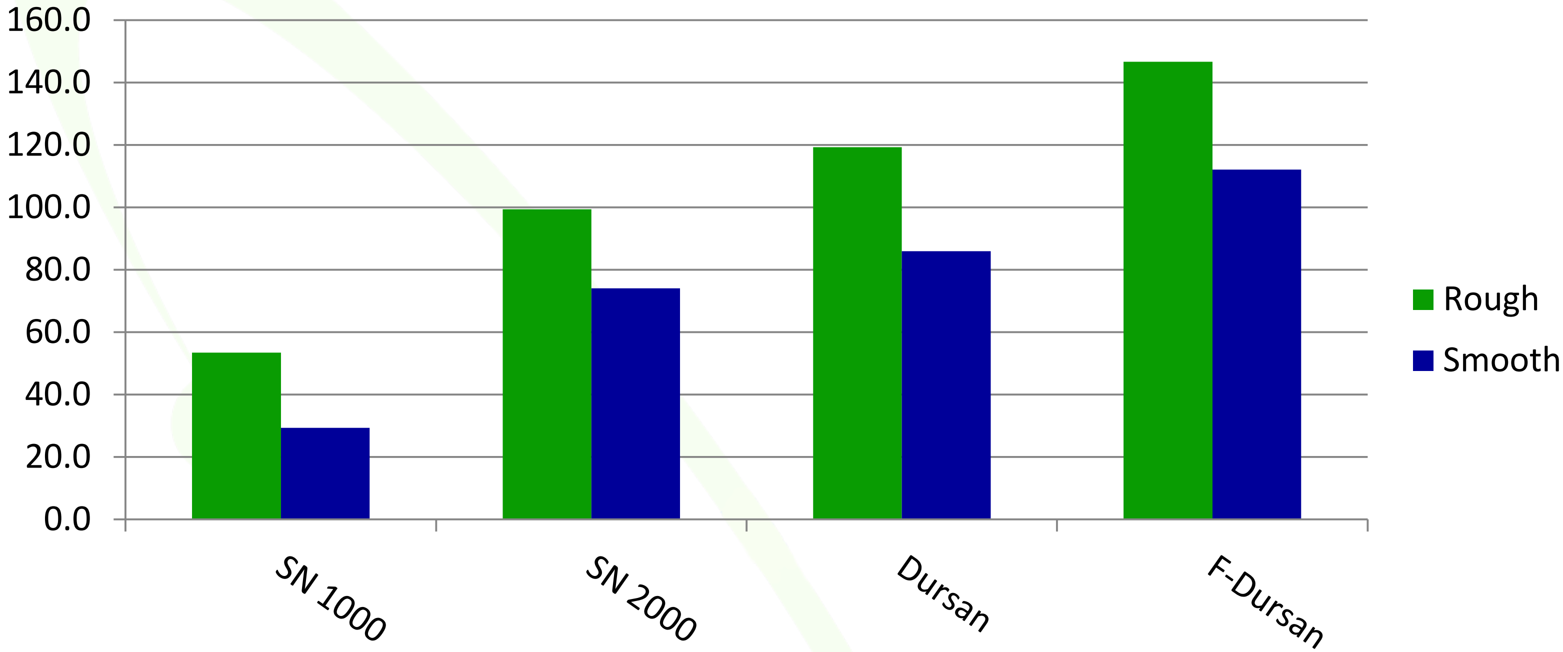
- Silver texture on copper with heptadecafluoro -1-decanethiol coating
- Air layer between water and metal coupon
- Critical viewing angle = 48.6° (same as water/air reflection boundary); <1% water in contact with surface (CA = 173°)

Larmour, I.A.; Bell, S.E.J; Saunders, G.C. *Angew. Chem. Int. Ed.* **2007**, *46*, 1710-1712.

Anti-Stiction

- Low energy surfaces
  - Hydrophobic
  - Oleophobic
- Fouling – Poor efficiency
  - Heat transfer
  - Flow restriction
  - Combustion efficiency
- Fluoro-functional Dursan

Properties and Performance: Hydrophobicity

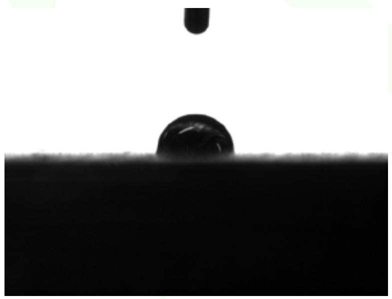


SN 1000	SN 2000	Dursan	FluoroDursan
49°	101°	121°	163°

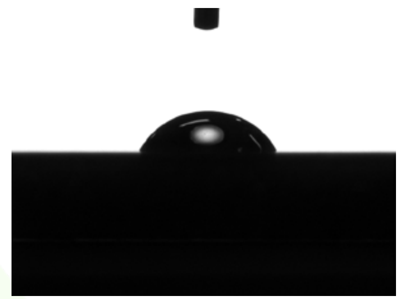
Rough Coupons

Rough: 120 grit; 58 rms (µin.)
Smooth: mirror-like #8; 10 rms (µin.)

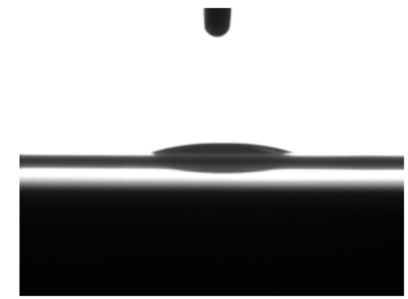
Oleophobicity studies on 316 SS Coated F-Dursan



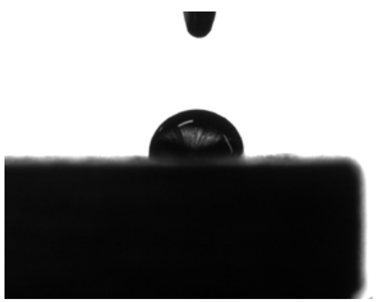
Hexadecane on rough
92.6°



Hexadecane on smooth
66.0°

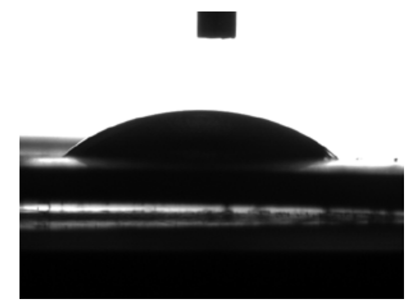


Hexadecane on Teflon
29.7°



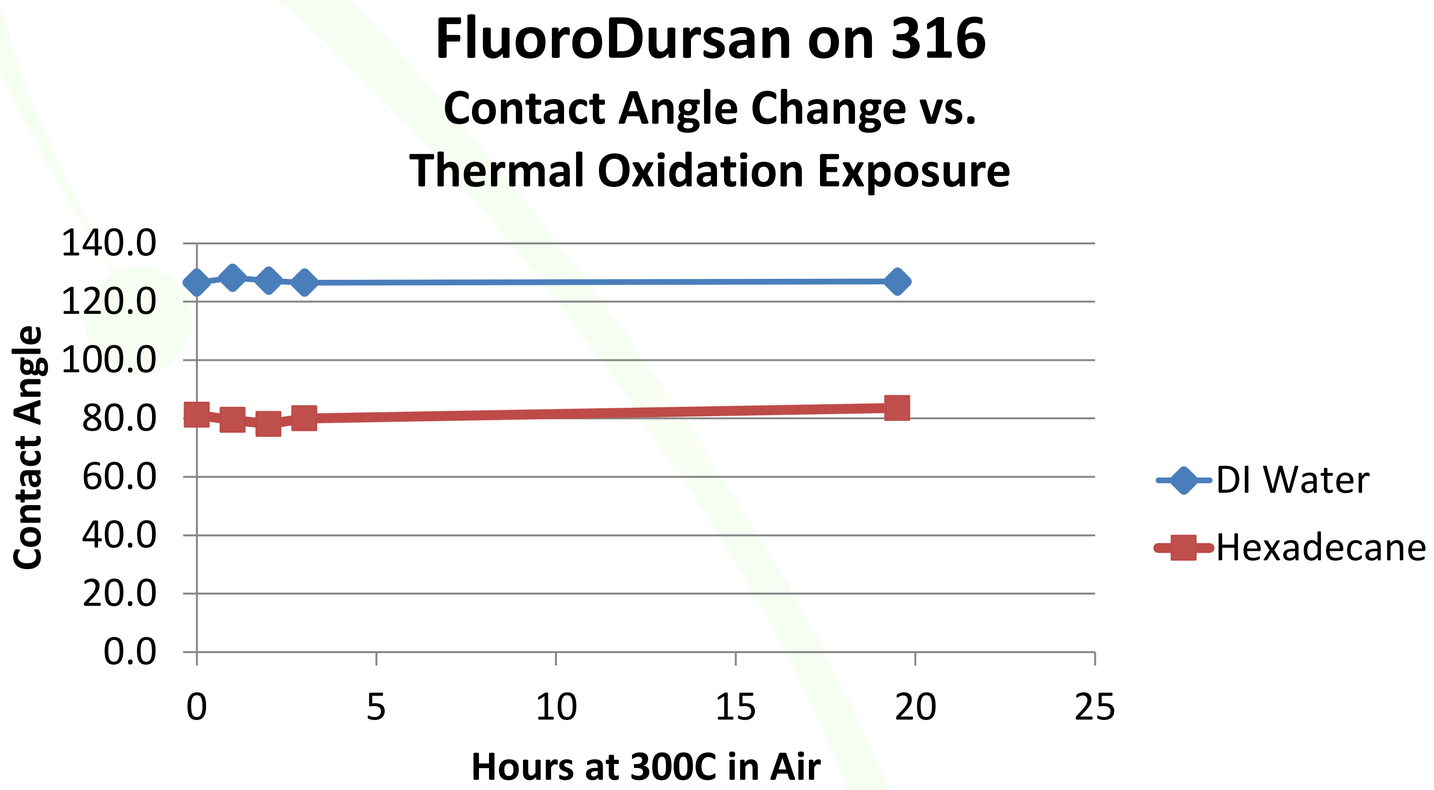
10W40 oil on rough
95.5°

10W40 oil on smooth
70.2°



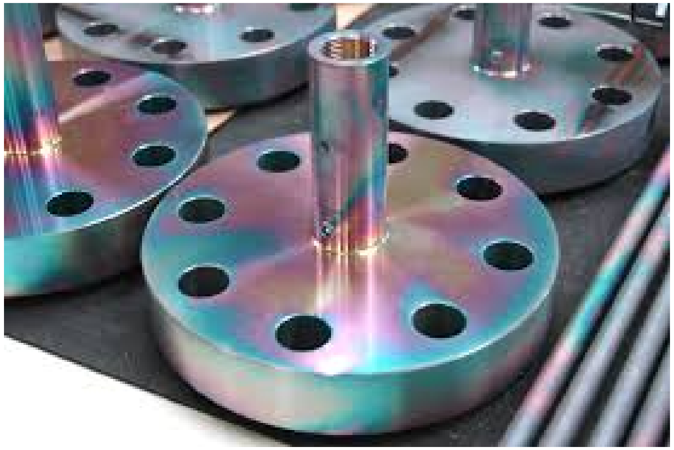
10W40 oil on Teflon
48.5°

Low Energy Surfaces: Hydrophobic / Oleophobic 316 SS



Conclusion

- Coatings are available for a wide range of applications
- Optimize based on desired property
    - Inertness
    - Corrosion Resistance
    - Anti-sticking
    - Purity



- Ultimate benefit is superior performance
    - Analytical results
    - Extend life
    - Reduce labor and capital cost
    - Improve efficiency
    - Optimize material selection and cost performance

Thank you!