Setting the Standard for Automation™

Coatings Improve Reliability and Accuracy of Sulfur, Mercury, Ammonia and NO_x

Mark Lawrence
SilcoTek Corporation

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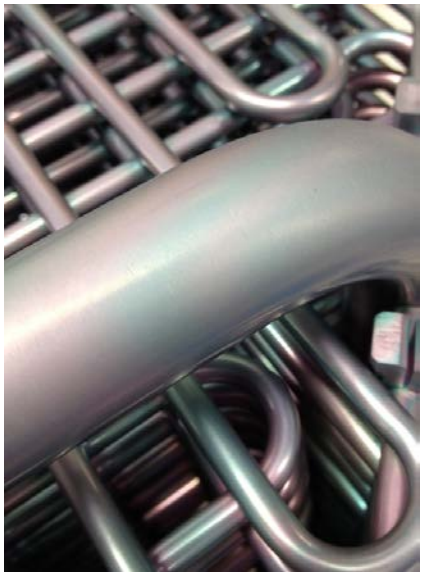
Presenter

- Mark Lawrence – Global Sales Manager for SilcoTek coatings. Earned his BS in Chemistry and an MBA from Penn State University. Has 20 years of experience working with coatings during employment at Restek Corporation and SilcoTek Corporation.

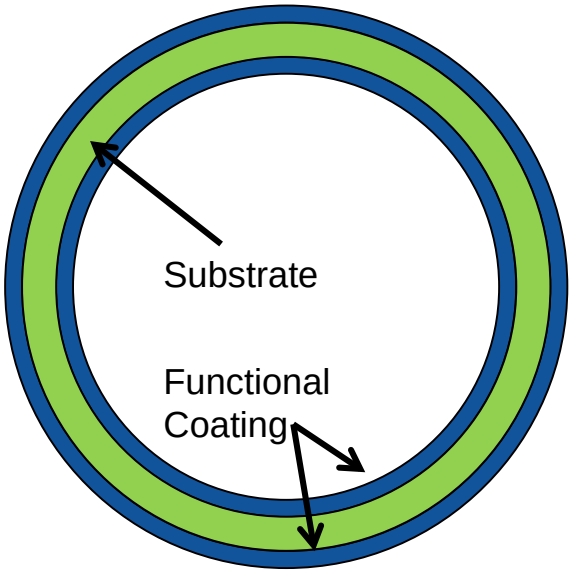
Introduction

- What are SilcoTek coatings
- Application use of coatings
- Field results and data
  - Flare Stacks
  - Down-hole sampling
  - Ethylene/propylene
  - Flue gas
  - Ammonia
  - NOx

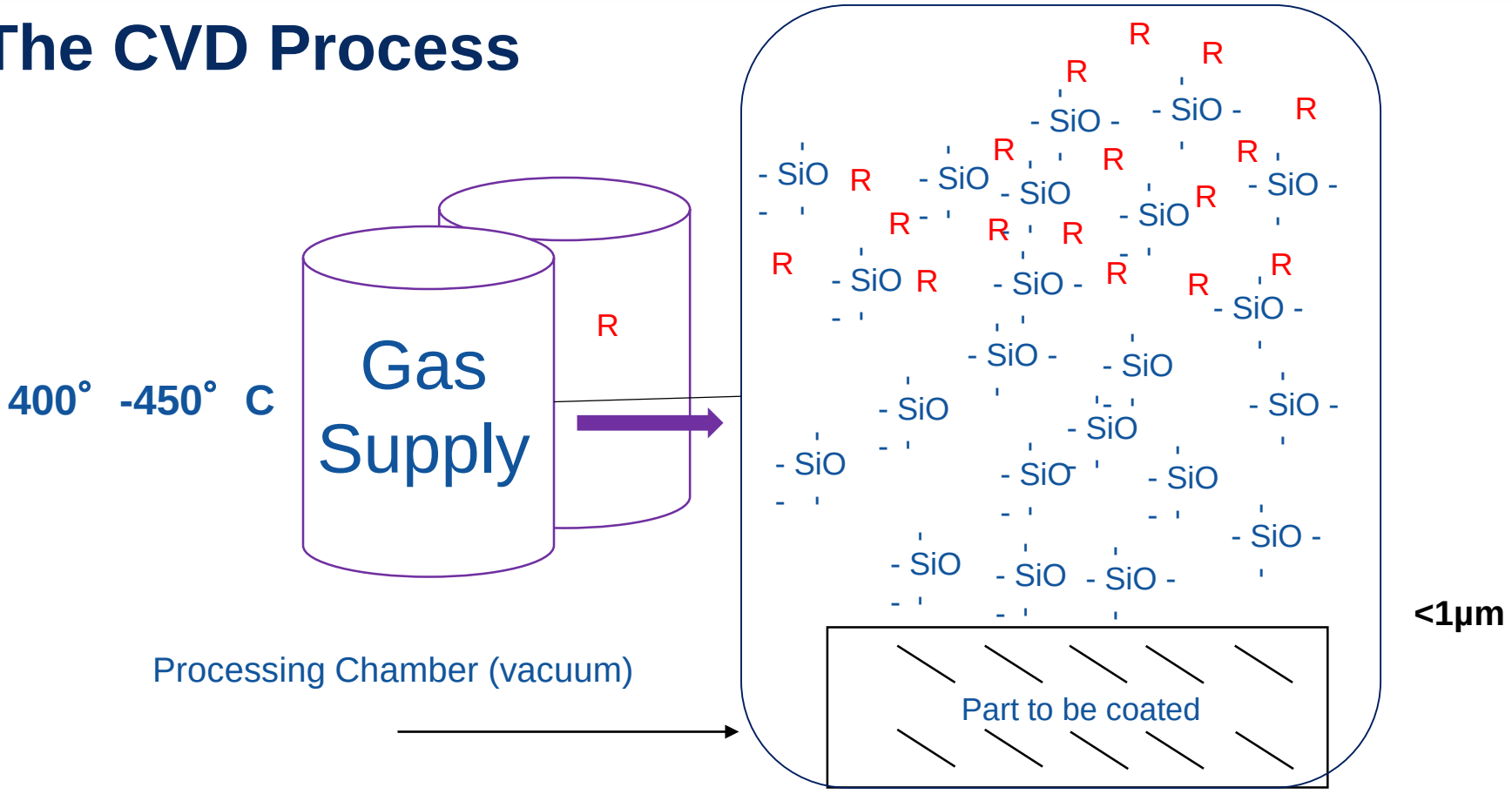


What we do

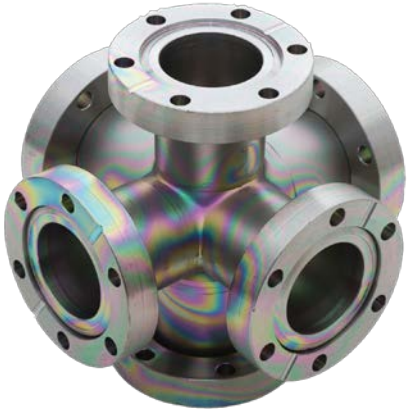
- Thermal decomposition of silanes onto substrates like stainless steel, titanium, super alloys, glass, ceramics, etc.
- Additional functionalization for more advanced surface properties
- Also able to directly functionalize substrate without coating



The CVD Process

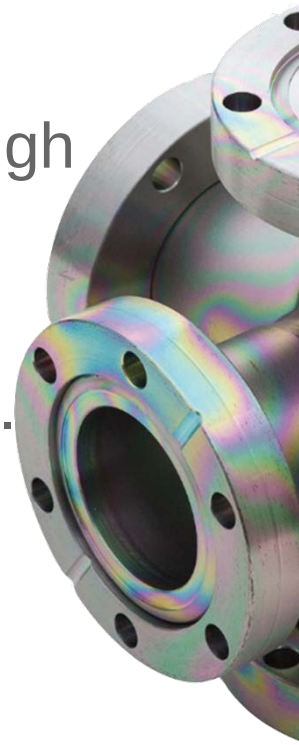


Technology



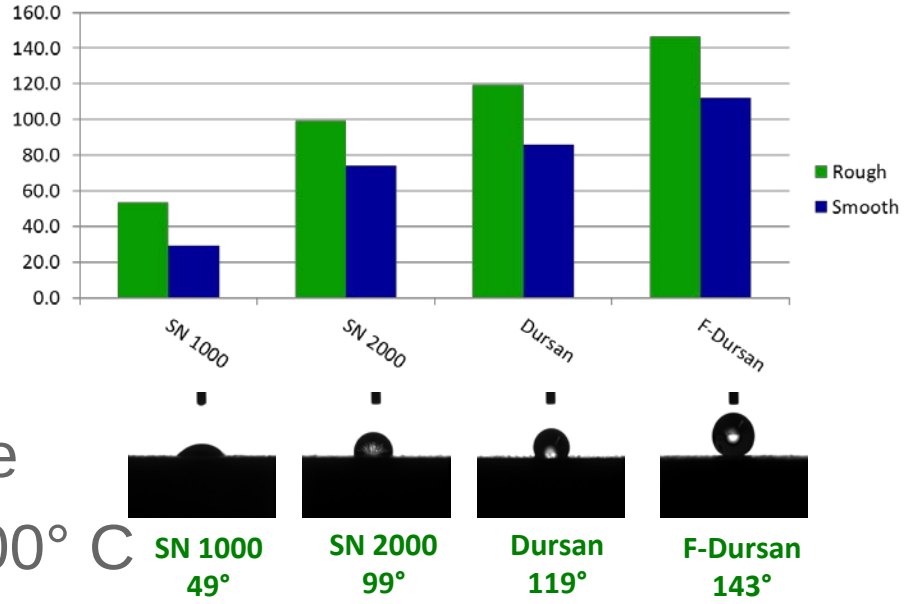
Advantages of CVD Coatings

- Non-line-of-sight deposition; uniformly treats 3D, high aspect ratio part geometries
- Molecular adhesion to base substrate. Won't flake.
- Scalable, versatile, and highly reproducible



Surface Properties

- Chemically inert / non-reactive
- Non-stick, high release
  - Hydrophobic
  - Oleophobic
  - Anti-fouling
- Oxidation resistant
- Corrosion resistant
- Dielectric or semi-conductive
- Stable at temperatures >1000° C



Common Applications

Analytical Chemistry	Oil and Gas Exploration
Refinery/Petrochemical	Semiconductor Manufacturing
Bio/Pharma	Automotive
Aerospace	Offshore
Chemical Manufacturing	Power Generation

Background

- SilcoTek first started using coatings in 1987 as part of Restek Corporation
- PTFE lined sample cylinders, fittings, tubing have a history of use in petrochem/refining for inert sampling
- ULSD & ULSG standards accelerated need for coated systems and components
- Needed alternatives to PTFE for high temperatures and high pressures to avoid delamination

Applications

Accurately Measure:

- Sulfur compounds
- Mercury
- Ammonia
- NOx / SOx

Uses of coatings

- Subpart –Ja, refinery flare gas testing
- Oil and Gas well down-hole sampling
- Ethylene/Propylene catalyst poisons
- Coal Fired Boiler Flue Gas testing
- Ammonia slip
- Automotive
- H_2S to SO_2 conversion above 100°C
- Tier 3 fuel standards

Flare testing: Sulfurs, Mercury, Ammonia

- Davidson, et. al.[4] published data on refinery flare gas monitoring systems performance over 1 year
- Monitoring range from 1 to 150,000 ppm total sulfur
- Vent gas measure at middle 50% of flare with angled coated probe to get representative sample
- Highlighted importance of stable instrumentation, heated sample system and inert coating to entire sample pathway
- Stream may even have HF from Phillips Alkylation units

Flare testing: Sulfurs, Mercury, Ammonia

- Lessons applied to Subpart –Ja demand
- Sample system stability:
  - Heated transfer lines
  - Surface finish considerations
  - Metallurgy
  - HF can be present

- Can achieve the regulatory standards and provide stable performance

Well Sampling: Mercury and Sulfur

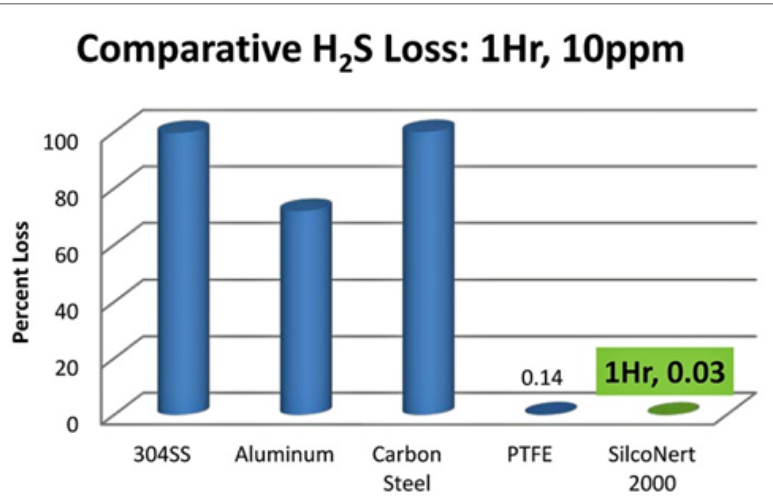
- Need to quantify sulfur and mercury content of wells
- Any level of mercury (measured in µg/m^3) is of interest because of mass volumes being pumped
- Presentation by Schlumberger in 2007[1] and 2013[5] highlight the application of coatings to create stable sample bottles.

Well Sampling: Mercury and Sulfur

- Conclusions:
  - Mercury necessitates clean handling and inert sample bottle or risk losing all mercury to adsorption
  - Sulfur results dependent on system design down-hole and of sample bottle conditions and composition on surface
  - Even 50ppm levels of Sulfur unstable in transfer unless coatings used to address adsorption created by metallurgy

Ethylene/Propylene: Trace sulfur

- Study by Biela, et. al. from Equistar and Air Liquide[6]
- Sulfur contamination causes catalysis poisoning which directly impacts yield
- H_2S (hydrogen sulfide) and COS (carbonyl sulfide) coming over in polymer-grade Ethylene and Propylene
- Conversion of COS in furnace to H_2S and then contact with catalysts
- Inert Sampling systems and stds are necessary for monitoring low level impurities to protect yields



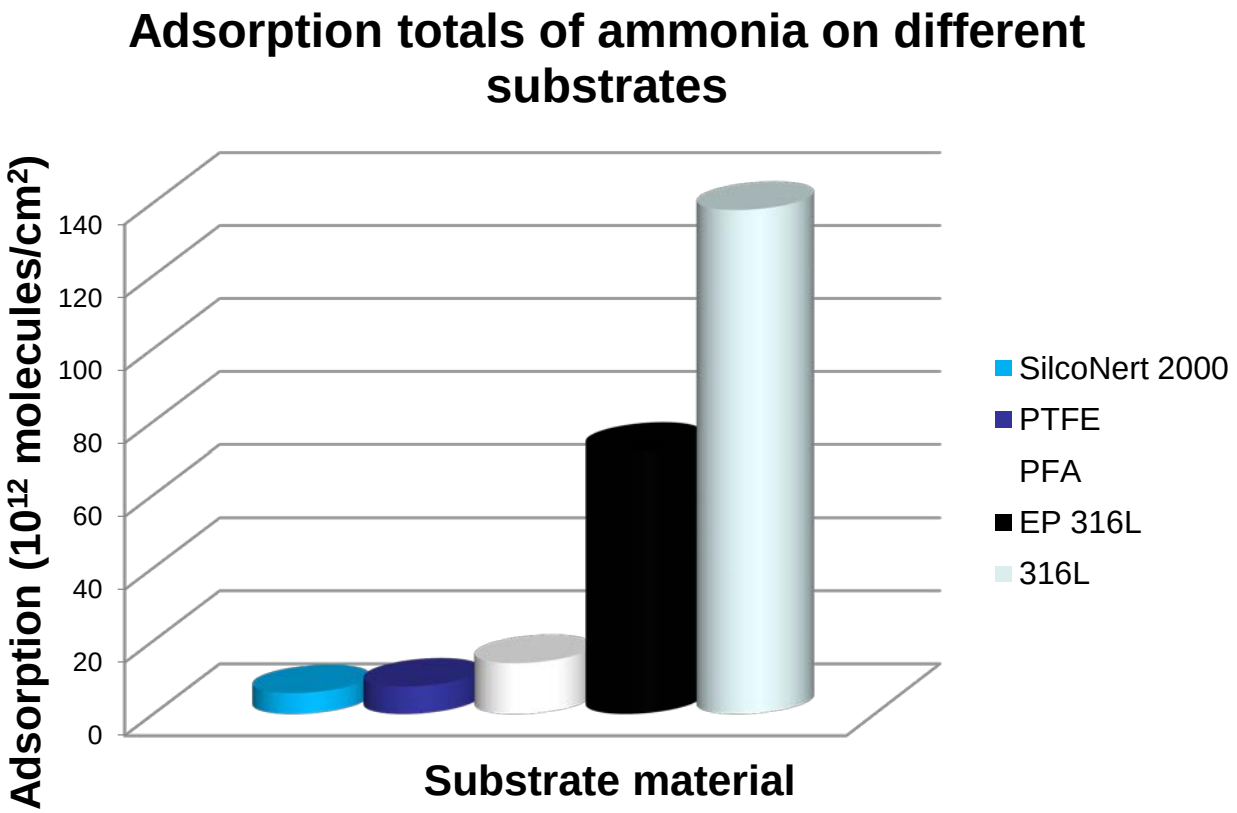
Flue Gas

- Emissions of mercury in Coal Flue Gas from Boilers is now a monitored pollutant. Also effluent from refining, petro activities that are monitored
  - Problem is the oxidation of mercury
    and inability to analyze due to loss.
- Elemental converted to HgCl2; HgBr2 (easier to scrub using carbon based adsorbents)
- Studies on oxidized mercury Hg^{2+} demonstrate 100% transfer of adsorptive compounds in coated transfer lines[7].

Ammonia

- Ammonia slip is release of ammonia through treatment process and pollution control equipment
- Necessary to accurately monitor the levels of ammonia
- Studies demonstrate surface roughness and use of inert materials or coatings greatly impacts ammonia transfer efficiency

Reducing adsorption of ammonia[8]



[8]Vaittinen, et. Al., "Adsorption of ammonia on metal and polymer Surfaces", University of Helsinki, 2013

NO_x compounds

- Common pollutant from combustion process
- Monitoring for boilers and automotive need to look at NO_x emissions.
- Mixed samples of NO_x compounds along with ammonia and moisture common for automotive exhaust, very difficult application
- Silco-based coating performing as well as PTFE-lined with no adsorption, change or loss[9]

H_2S Conversion above 100°C

- H_2S decomposing on hot stainless steel as demonstrated by Biela, et. al.[6] and Reese, et. al.[10]
- Mechanism

$$2H_2S + 2O_2 \rightarrow 2H_2O + \frac{1}{n}S_n + SO_2$$

- Biela demonstrated complete loss of H_2S, 100ppb, at temperatures above 100°C
- Biela demonstrated when inert coating applied on SS, H_2S loss is eliminated. Testing conducted from 50°C to 225°C

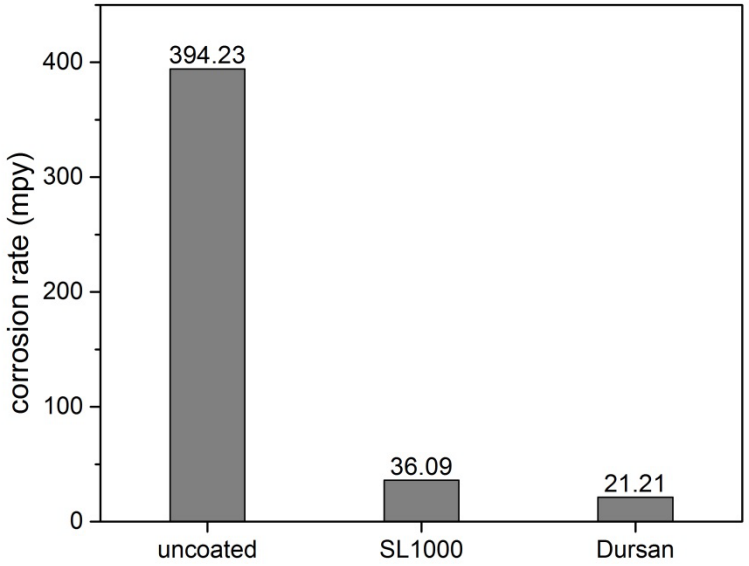
[10] Reese, G.; Mason, A.; Cuthbert, D.,"A Novel Solution for the Analysis of Speciated Sulfurs and Nitriles in Various Hydrocarbon Streams"; Gulf Coast Conference, Galveston, TX, Paper 36 (2014)

Corrosion Capabilities

85% H_2SO_4 at 80°C

- Uncoated coupon showed severe corrosion after a 7-hour immersion.
- Coatings reduced corrosion by over 10x.
- Dursan provided better protection than Silcolloy under this condition.
- **Dursan and Silcolloy both provide benefits and reduce corrosion by 10x .**

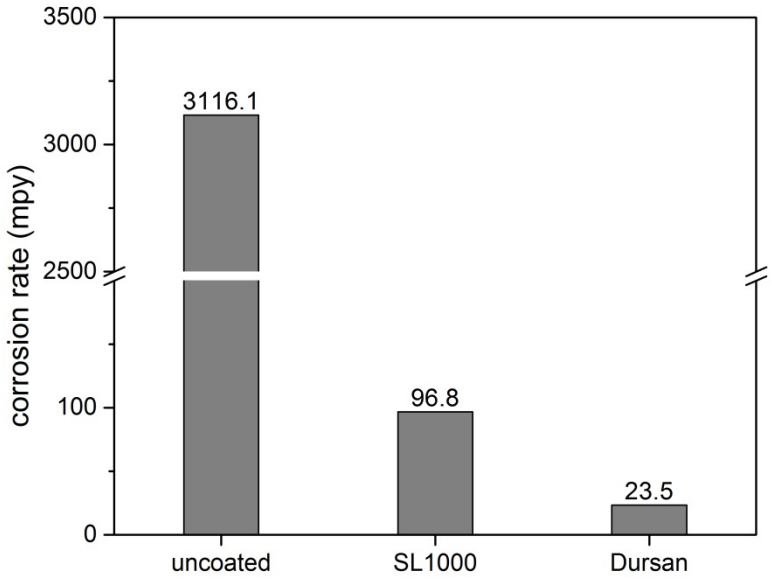
uncoated SL1000-coated Dursan-coated



6M HCl (18 wt%) at 50°C

- Uncoated coupon had severe corrosion after a 7-hour immersion at 50°C.
- Coating greatly delayed and reduced corrosion.
- Dursan outperformed Silcolloy in this test.
- **Dursan offers great benefits under this condition.**

uncoated SL1000-coated Dursan-coated



Conclusion

- Trace and active compound analysis are getting more accurate and reliable through coatings
- Customers are demanding better results at lower levels
- Smoother substrates help analysis, coatings can further increase accuracy and detection limits of sampling techniques
- The technology is there and there are experts at all OEM's deploying improved equipment.
- As more requirements emerge, more technologies are going to be required to meet the growing standards of a changing world, especially outside the U.S.A.