Coatings Improve Reliability and Accuracy of Sulfur, Mercury, Ammonia and NO$_x$

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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

Gas Supply

Processing Chamber (vacuum)

400° - 450° C

<1μm
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

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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
- H₂S to SO₂ conversion above 100°C
- Tier 3 fuel standards
Flare testing: Sulfurs, Mercury, Ammonia

- Davidson, et. al.\textsuperscript{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

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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
• Need to quantify sulfur and mercury content of wells
• Any level of mercury (measured in µg/m³) is of interest because of mass volumes being pumped
• Presentation by Schlumberger in 2007¹ and 2013⁵ highlight the application of coatings to create stable sample bottles.
• 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
- Sulfur contamination causes catalysis poisoning which directly impacts yield
- H₂S (hydrogen sulfide) and COS (carbonyl sulfide) coming over in polymer-grade Ethylene and Propylene
- Conversion of COS in furnace to H₂S 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 Hg²⁺ demonstrate 100% transfer of adsorptive compounds in coated transfer lines⁷.
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

Adsorption totals of ammonia on different substrates

- SilcoNert 2000
- PTFE
- PFA
- EP 316L
- 316L

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$_2$S Conversion above 100°C

- H$_2$S 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$_2$S, 100ppb, at temperatures above 100°C
- Biela demonstrated when inert coating applied on SS, H$_2$S 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% $\text{H}_2\text{SO}_4$ 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.**
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.**
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.