Characterizing the Performance of Surface Modifications that Enhance Sensitivity, Reliability, Reproducbility and Accuracy of Analytical Instruments

Technical Insight

Authors

Gary Barone, Business Manager

Dr. David Smith, R&D Scientist

Marty Higgins, Business Development

SilcoTek® Corporation

Background

Process analyzers used in refining, petrochemical and off-shore environments are often exposed to corrosive chemicals such as sulfuric acid, hydrochloric acid, caustic streams and/or salt water. They are required to withstand these corrosive conditions while maintaining chemical inertness for the sampling of adsorptive chemicals such as reduced sulfur compounds.

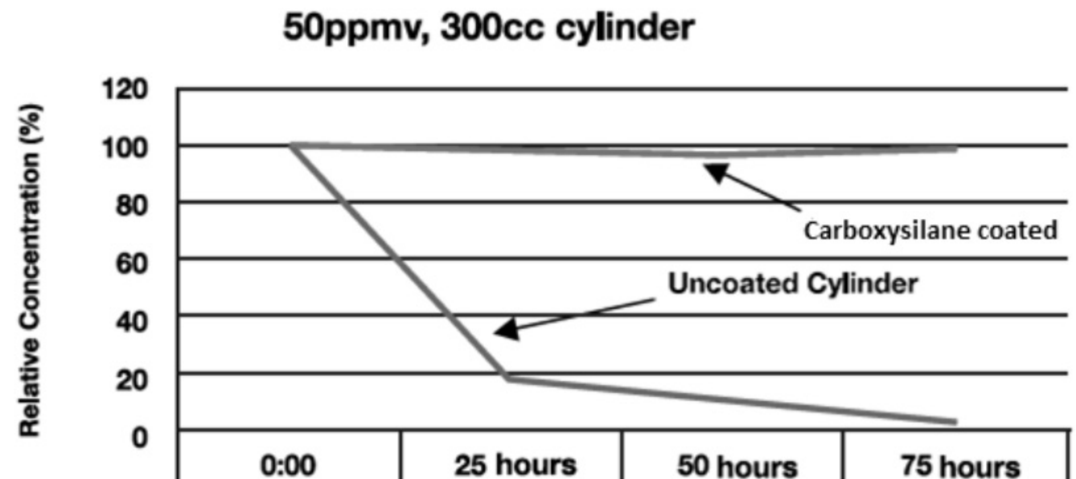
Stainless steel materials used to construct these analyzers, if uncoated, exhibit high activity towards these sulfur compounds, and can easily corrode under harsh chemical conditions, which will further compound the reactivity issue. This paper presents laboratory corrosion and chemical inertness test results of SilcoTek's CVD coatings, and evaluates their performance in environments common to the petrochemical, refining and off-shore industries.

Discussion and Data

Bare stainless steel surfaces strongly adsorb sulfur compounds such as hydrogen sulfide, carbonyl sulfide and mercaptans. Figure 1 below shows the degradation comparison of 50 ppm H_2S gas stored in an uncoated stainless steel (SS) cylinder versus in a SilcoTek® Dursan®-coated stainless steel cylinder, over the course of 75 hours. The uncoated SS cylinder suffered near total loss of H_2S at the end of 75 hours, whereas the Dursan-coated cylinder maintained excellent recovery rate over the same period of time. Note that Dursan is SilcoTek's tradename for the carboxysilane coating referred to in Figure 1.

Figure 2 shows the degradation comparison of 17 ppb H_2S gas stored in an uncoated SS cylinder versus in a SilcoTek SilcoNert® 2000-coated SS cylinder. Again the loss of H_2S on bare SS is rapid and irreversible, which drops to zero within 24 hours (1 day), while the SilcoNert 2000-coated cylinder remained exceptionally stable over the test period of 7 days. Note that SilcoNert 2000 is SilcoTek's tradename for the modified silicon coating referred to in Figure 2.

Using these inert coatings on analyzer components eliminates the need for traditional flow-through passivation techniques, and produces very reliable, stable and reproducible analytical results. The SilcoNert 2000 coating has been successfully used in trace analysis of ppm and ppb levels of sulfurs, moisture, ammonia and down to pptr levels of mercury. It is the most inert coating offered by SilcoTek. The Dursan coating has been successfully used in ppm levels of sulfur and moisture analyses, and also offers better corrosion resistance and mechanical wear resistance than the SilcoNert 2000 coating.



	0:00	25 hours	50 hours	75 hours
Stainless Steel	100	19	10	4
Carboxysilane	100	98	96.6	98.3

Figure 1: Hydrogen sulfide (H_2S) at 50 ppmv in Dursan-coated cylinders is stable over a period of 3+ days, while the same sample in an uncoated stainless steel cylinder is rapidly lost due to adsorption of the H_2S compounds.

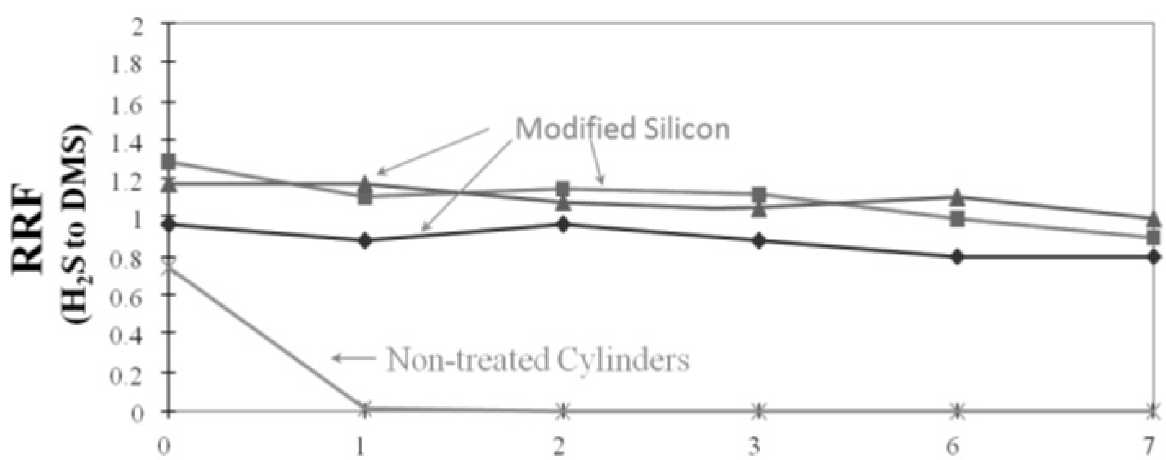


Figure 2: Hydrogen sulfide (H_2S) at 17 ppbv in SilcoNert 2000-coated cylinders is stable over a period of 7+ days, while the same sample in an uncoated stainless steel cylinder is completely adsorbed after only one day.

One of the unique beneficial characteristics of the Dursan® coating is its hydrophobicity, or resistance to moisture. The coating exhibits an advancing contact angle of 105.5° and a receding angle of 85.3° with DI water. A hydrophobic surface will dry quicker and result in an analytical system that is more reliable and reproducible, as moisture on sampling systems can produce poor stability of active compounds.

The Dursan coating also provides excellent corrosion resistance on a stainless steel substrate. Table 1 below summaries the results obtained from ASTM G31 immersion tests performed with a variety of acids for 24 hours at 22°C and under room pressure. Three samples were tested in each configuration and the average corrosion rate value was reported.

Lastly, the Dursan coating provides better wear resistance than the SilcoNert® coating and the bare SS substrate. Data generated from ASTM G133 pin-on-disk measurement indicates that the Dursan coating reduces the wear rate of bare 316L SS (13.81 x 10^{-5} mm^3/Nm) by half, to 6.13 x 10^{-5} mm^3/Nm, as the average coefficient of friction reduces from 0.589 for uncoated SS to 0.378 for Dursan-coated SS.

corrosion rate in mpy (mils per year)	6N HCl	6N HBr	25% H_2SO_4	concentrated HNO_3	85% H_3PO_4	5% HF
bare 316L SS	114	3.4	54.6	0.78	0.62	120
Dursan-coated 316L SS	2.7	0.8	5.4	0.1	0.08	80.4

Table 1: Dursan®-coated 316L SS substantially improves corrosion performance over uncoated 316L SS in various acids per ASTM G31 guidelines.

In summary, SilcoTek's CVD coatings have demonstrated improved reliability and durability while tightening the reproducibility of data generated on analytical systems. The SilcoNert® 2000 coating offers extreme inertness to ppb levels of trace analysis, whereas the Dursan® coating offers a combination of chemical inertness at ppm levels as well as corrosion resistance, hydrophobicity and wear resistance.

References

1. Jahnke, J., "An Operator's Guide to Eliminating Bias in CEM Systems", Technology Associates, Research Triangle Park, North Carolina, U.S. Environmental Protection Agency Acid Rain Division, Washington, DC, Contract number 68-D2-0168, 1994.
2. Barone, G., Higgins, Smith, D."The use of Coatings to Improve the Physical and Analytical Reliability of Process Monitors used with Ammonia, Mercury and Hydrogen Sulfide Containing Streams", Presented as Paper 99 at the Gulf Coast Conference, Galveston Island, TX, October 17, 2012.
3. Sulyok, M., Harberhauer-Troyer, C., et al., "Investigation of the Storage Stability of Selected Volatile Sulfur Compounds in Different Sampling Containers" J. Chromatogr. A 917(1-2), pgs. 367-374 (2001).
4. Davidson, T., Limfueco, R., et al., "Performance of Environmental Monitor for Total Sulfur and High Heating Value of Refinery Flare Vent Gas Systems", ISA AD 2011, The 56th Annual Symposium of the Analysis Division, League City, TX, 2011.
5. Winkler, K., "Amine Monitoring with PTR-MS" Internal Study Report, Ionimed Analytik GmbH, June 2011.
6. Barone, G., Higgins, M., "Comparison of Surface Composition on Stability of Mercury Transfer and Holding", Electric Utility Environmental Conference, Tucson, AZ, 2008.
7. ASTM G31-12a, "Standard Guide for Laboratory Immersion Corrosion Testing of Metals", 1972.
8. ASTM G133-05, "Standard Test Method for Linearly Reciprocating Ball on Flat Sliding Wear", 2010.
9. Tchon, J., "Analytical Report: Nanovea –TRB101217-30", Nanovea Corp, Internal study report, December, 2010.
10. Barone, G.; Higgins, M. "Improving the Reliability of Analytical and Sampling Systems in Challenging and Corrosive Environments" ISA AD 2011, The 56th Annual Symposium of the Analysis Division, League City, TX, 2011.