

# Use of Inert, Corrosion Resistant CVD Coating for Oil and Gas Service

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## ABSTRACT

As growth in demand for petroleum products continues to drive an increasingly diverse supply, challenges involved with the exploration, extraction, transportation and testing of oil and gas have pushed companies to manage costs, primarily via corrosion control. However, with additional requirements including enhanced wear resistance and chemical sampling inertness, finding a suitable yet economical solution is especially daunting.

The use of advanced, high performance protective coatings is gradually becoming an industry-wide solution for meeting both performance and financial expectations. This paper will introduce a silicon-oxygen-carbon coating (Dursan®) as one such advanced treatment. Following an introduction to proper coating selection criteria, the acidic corrosion resistance, wear resistance, and chemical inertness of this chemical vapor-deposited (CVD) coating will be compared to that of other common surface treatments used in oil and gas sampling service.

**Keywords:** coating, corrosion control, H<sub>2</sub>S, inertness, sampling

## 1 INTRODUCTION

Sulfur compounds, particularly hydrogen sulfide (H<sub>2</sub>S), naturally occur at trace levels in most oil and natural gas reservoirs worldwide. Quantifying the H<sub>2</sub>S content i.e. “sweetness” of potential yields is critical to understanding product purity; high H<sub>2</sub>S content (generally greater than 0.5%) indicates a “sour” yield that requires additional purification. However, the steels, stainless steels, and exotic alloys which are commonly used in the flow paths of well sampling equipment have proven to adsorb certain sulfur compounds, making accurate, low-level quantification of these molecules impossible [1]. This, coupled with corrosive extraction environments and increasingly strict government regulations, has driven an overwhelming need for the development and use of surface modifications on sample storage and analysis equipment.

Over the years, many solutions have been developed to enhance sampling system compatibility with reactive compounds like H<sub>2</sub>S and mercury (Hg), such as polytetrafluoroethylene (PTFE), siloxane, and chemical vapor-deposited silicon-based coatings. The complex sampling requirements discussed above prove that no single solution exists, but pairing a high performance coating with proper base material selection will ensure a reliable quantification of oil and gas yield composition i.e. quality.

## 2 DISCUSSION

Prior to the full scale development of an oil or natural gas field, samples must be collected and accurately analyzed to ensure the supply is suitable. The substrate material used for most sampling flow path equipment (sample cylinders, valves, filters, etc.) is traditionally stainless steel or other metal alloys as dictated by physical and design parameters like temperature, chemical exposure, and pressure ratings. A variety of these materials meet the physical requirements of a sampling system but fail to provide the chemical inertness necessary for trace level detection of critical compounds such as H<sub>2</sub>S.

### 2.1 Sulfurs (H<sub>2</sub>S) and Steels/Exotic Materials

In addition to surface area, temperature and pressure exposure, the chemical composition of a metal substrate will affect the type of reactions that occur with analytes in the sample that move through the flow path. 316L stainless steel is a commonly specified material for sampling componentry due to its ability to form a stable and protective oxide layer. However, highly-reactive free iron (Fe) on the surface poses analytical problems; an ASTM A380 “Ferroxyl Test for Free Iron” demonstrates that the surface’s iron and iron oxides are readily attacked, providing avenues for both corrosion and increased surface activity under the harsh conditions typically found in oil and gas sampling service [1]. Over time, due to steady adsorption of sulfurs like H<sub>2</sub>S, the surface will reach a near-stable equilibration point and make trace-level quantification impossible.

This phenomenon is even more apparent when copper-containing superalloys like Monel® are used in place of stainless steel to combat harsh corrosives. H<sub>2</sub>S and other sulfur compounds are completely scrubbed from sample streams constructed from these materials; Hashem, et al. have proven that samples at 50 parts-per-million (ppm) are scavenged in Monel® tubing lines and no aforementioned equilibration effects occur [2]. It is clear, then, that surface modifications i.e. advanced coatings must be used in conjunction with suitable base materials to ensure the analytical results from oil and gas field qualification tests are exhaustive and error-free.

### 2.2 Selection of Coatings

The variety of materials available to solve sampling system compatibility problems are listed in Table 1. Some are specific to pH range tolerances while others provide higher

thermal stability or specially-tailored surface chemistry specific to certain critical analytes.

Coating	Composition
PTFE or PFA	100% polytetrafluoroethylene or perfluoroalkoxyacetyl
Siloxane	polydimethylsiloxane
a-Si	amorphous silicon
a-Si-R; R=(C-H)	hydrocarbon-functionalized amorphous silicon
a-SiOC (Dursan)	carboxysilicon

Table 1: Common commercial coatings and compositions

Selection of required material properties is often derived from the most significant failure mode in the application. Abrasion and wide pH exposure in oil and gas sampling applications limit the potential coating solutions that can be used. For example, significant wear or vibrations result in poor performance for PTFE coatings, however PTFE is one of only two options discussed here that is suited for pH 0-14. Table 2 summarizes some of the most important physical characteristics for coatings in oil and gas service.

Property	Dursan	a-Si-R	a-Si	Siloxane	PTFE or PFA
Maximum temp.	450° C	450° C	1400 ° C	250° C	260° C
Minimum temp.	-210° C	-210° C	- 210° C	-40° C	-240° C
Low pH limit	0	0	0	2	0
High pH limit	14	7	7	7	14
Thickness	2µm	0.5µm	0.5 µm	0.5µm	25µm
Adhesion	Very good	Very good	Very Good	Good	Poor

Table 2: Physical properties of coatings

The final and most critical criterion to the selection of an appropriate coating for sample stream components is the chemical compatibility of the coating with critical compounds and corrosive media involved in the sample extraction process. Table 3 briefly summarizes the coatings' compatibility in common sampling applications (note: <ppm levels of H<sub>2</sub>S and Hg). Inertness in these applications is critical for accurate qualification of oil and gas fields and, additionally, mitigating potential corrosion. These factors have a significant impact on both the quality of the final product and the project's bottom line.

Coating	H <sub>2</sub> S Sampling	Hg Sampling	High pressure sampling	Chloride Containing
PTFE or PFA	X	X		X
Siloxane				
a-Si			X	X
a-Si-R; R=(C-H)	X	X	X	
a-SiOC (Dursan)	X		X	X

Table 3: Compatibility of coatings

It is clear that, specifically for sampling potential oil and natural gas yields, only PTFE/PFA and the amorphous silicon-based coatings are suitable for maintaining an inert barrier between trace levels of H<sub>2</sub>S and the metal substrate. Further, only the Dursan coating exhibits the necessary combination of robustness and chemical inertness for repeated, reliable sampling of H<sub>2</sub>S in the abrasive conditions present in oil and gas fields. The subsequent sections of this paper will demonstrate Dursan's chemical inertness, corrosion and wear resistance properties.

### 3 EXPERIMENTAL - DURSAN® COATING

SilcoTek® Corporation's Dursan is a chemical vapor-deposited (CVD) coating comprised of amorphous silicon, oxygen and carbon. Unlike traditional dip or spray coating techniques, CVD is a non-line-of-sight vacuum process which ensures all blind holes and complex geometries are coated. Additionally, unlike PTFE, the coating is physically deposited into the lattice of the base metal, leading to full adhesion and the ability to bend coated parts without risk of flaking. The composition of Dursan and its diffusion into a stainless steel substrate are illustrated in Figure 1 via Auger Electron Spectroscopy (AES).

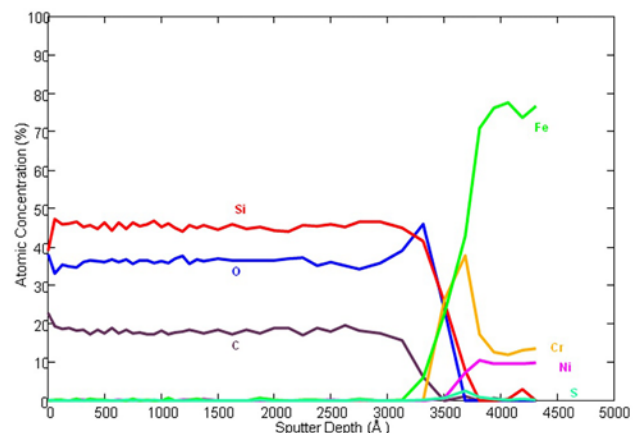


Figure 1: AES profile of Dursan coating

### 3.1 Inertness to Hydrogen Sulfide (H<sub>2</sub>S)

Hydrogen sulfide (H<sub>2</sub>S) is the most critical active compound requiring quantification in crude oil and natural gas extraction. Yields containing more than a few ppm of H<sub>2</sub>S are considered “sour” and must be purified. Figures 2 and 3 demonstrate the need for an inert coating during the sampling, storage and analysis of this highly active analyte. Non-treated sampling components begin to adsorb the H<sub>2</sub>S compounds immediately as described previously in section 2.1. Dursan-coated containers provide sample stability and a realistic time frame for transporting the sample to the laboratory without degradation or loss.

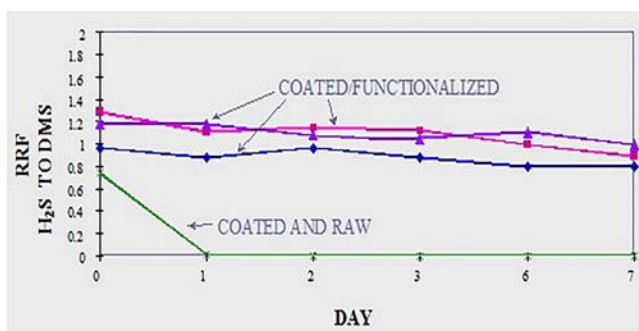


Figure 2: Sulfur compounds at 17 ppbv in Dursan-treated stainless steel containers

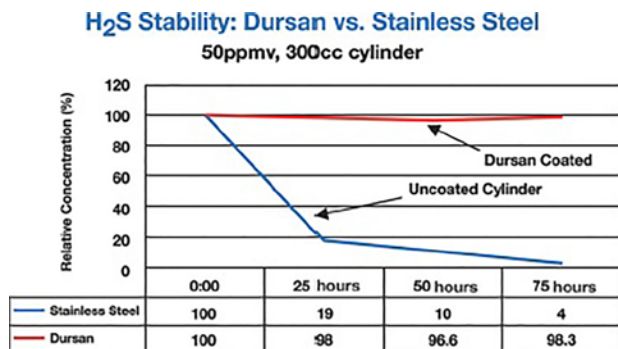


Figure 3: H<sub>2</sub>S compounds at 50 ppm in Dursan-coated stainless steel containers versus non-treated containers

As demonstrated, the degradation of H<sub>2</sub>S on bare stainless steel is rapid and irreversible. Both at 50 ppm at 17 ppbv levels, H<sub>2</sub>S is lost within 24 hours, making an effective analysis practically impossible due to transportation time between field and laboratory. It is worth noting that, in work to test the stability of sulfur compounds during such static sampling, the use of gases like silane (SiH<sub>4</sub>) along with multiple day exposure to 5000 ppm H<sub>2</sub>S was required to create a passive cylinder for storage [3]. Much of the data in these studies were gathered to demonstrate stability

for the use of creating low-level H<sub>2</sub>S standards in fuel. Commercially available Dursan-coated components have eliminated this need for passivation and are now recognized as “out of the box” solutions for sulfur sampling and transport. This eliminates the need for working with dangerous materials such as high concentrations of H<sub>2</sub>S or pyrophoric gases such as silane.

### 3.2 Corrosion Resistance

Chloride environments and chloride-containing oil and gas supplies are common in exploration workflows. The aforementioned surface treatments in addition to exotic materials all have been used to increase the lifetime of components in these corrosive applications. Table 4 provides the results obtained from ASTM G31 testing, comparing Dursan to an a-Si coating and bare 304 stainless steel. This method is an immersion test for 24 hours in a 6M HCl (18%) solution at room temperature and pressure. After immersion, differential weighing allows determination of the amount of material loss. The sample size for each configuration was 3 samples. The a-Si coated stainless steel shows greater than 20 times the resistance of non-treated 304 stainless steel in this environment while the Dursan treatment creates greater than a 200 time improvement. Any loss whatsoever in the coated samples occurred as a result of pitting corrosion. The pitting is an indication that there are still pin-holes present in the surface which allowed corrosive attack to initiate.

24hr; 6M HCl; 22° C	304 SS	a-Si coated	Dursan coated
MPY (mils-per-year)	389.36	16.31	1.86
Improvement Factor	---	23.90	209.8

Table 4: Sample weight loss after 24 hour exposure to 6M (18%) HCl

### 3.3 Wear Resistance

A final factor for consideration in selecting an appropriate surface treatment for making trace level H<sub>2</sub>S sampling possible is the coatings’ wear resistance. Down-hole sampling equipment is often subjected to significant abrasion from repeated deployment and retraction in the field. This exposure can easily remove an a-Si coating or crack PTFE/PFA coatings in only one use. To that effect, wear resistance is desired in order to avoid frequent and costly replacements. Table 5 summarizes the data obtained from wear studies conducted on both non-treated and treated surfaces. Data were generated using a pin-on-disk tribometer (Nanovea, Irvin, CA). The experiment uses a flat plate loaded onto the test rig and the indenter applies a precise force to surface. The plate is then rotated and forces

are measured between the pin and the disc. Results from this experimental method can produce wear behavior and friction coefficients of the plate surface [4]. Results from this experiment demonstrate that the Dursan coating wears less than untreated steel and an a-Si or a functionalized a-Si coated surface. The improved wear resistance of the substrate as a result of the coating leads to longer lifetimes of oil and gas down-hole sampling equipment while drastically reducing the number of required replacements.

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<b>Pin on Disc; 2.0N</b>	<b>316 stainless steel</b>	<b>Dursan coated 316 stainless steel</b>	<b>a-Si coated 316 stainless steel</b>
<b>Wear rate (x10<sup>-5</sup>mm<sup>3</sup>/Nm)</b>	13.810	6.129	2
<b>Improvement Factor over Stainless Steel</b>	---	2 times	1/3 times

Table 5: Wear resistance of coatings

## 4 CONCLUSION

Today, coatings are well-accepted means for drastically improving the performance characteristics of steels and metal alloys used for oil and gas service. While the corrosion resistance of untreated alloys may suffice for traditional exploration and extraction methods, these surfaces must be enhanced in order to make them suitable for analyzing trace levels of impurities, namely hydrogen sulfide (H<sub>2</sub>S), in crude oil and natural gas yields. Offering a combination of chemical inertness, corrosion resistance and wear resistance, these coatings have different limitations depending on the base substrate. The Dursan® coating outlined in this paper offers the required inertness for accurate quantification of H<sub>2</sub>S and other compounds, while also demonstrating physically robust qualities that alternatives such as PTFE/PFA lack. Regardless of the surface treatment that is used, the ability to accurately evaluate the contents of oil and gas fields will continue as an increasingly specified requirement.

## REFERENCES

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