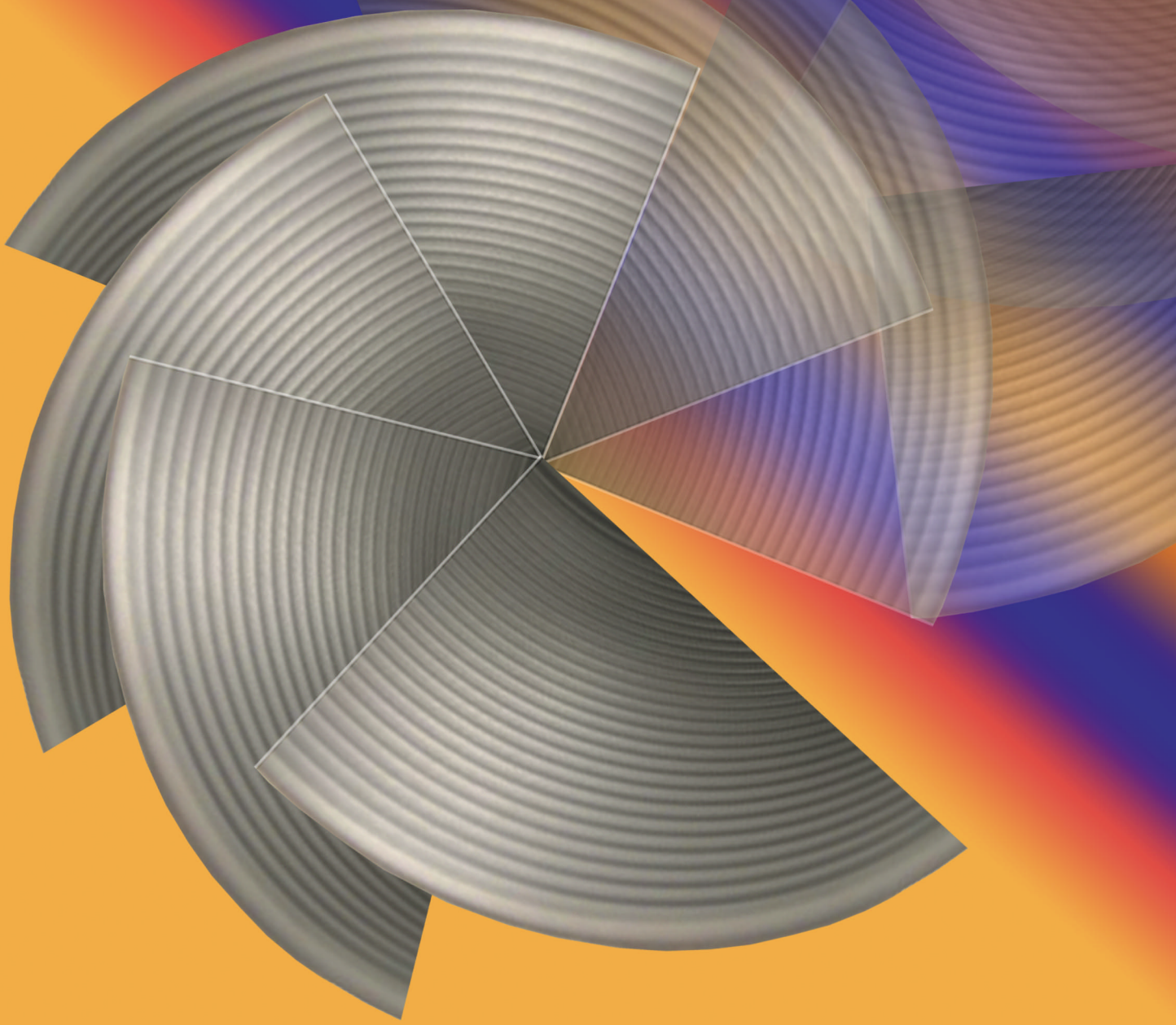
# Pipe Coating Technologies Tackle Corrosion and Wear for Oil & Gas Industry



By William Boardman, Andrew Tudhope, Tom Casserly and Deepak Upadhayaya
Sub-One Technology, Pleasanton, CA 94588

According to the Energy Information Administration's International Energy Outlook for 2006, world oil demand is expected to grow from 80 million barrels per day in 2003 to 98 million barrels per day in 2015 and 118 million barrels per day in 2030. On average, the United States accounts for one-fourth of global oil consumption using approximately 20.3 million barrels per day in 2005.[1] While the U.S. is the leading consumer of the world's oil, its own oil supply is dwindling. Oil and gas companies, domestically and abroad are forced to drill deeper, often in off-shore locations. The drilling environments are harsh and the crude oil produced is much more corrosive. While the environmental and chemical challenges mount, advancements with materials and corrosion-control technologies have not kept pace. In fact, pipe material and coating technology hasn't changed much since the 1970s. In August 2006, the U.S. oil industry experienced first-hand the problems caused by, and cost implications of corrosion, casting a spot light on the need for innovation in pipe coating materials and processes.

## Old Tricks for Today's Challenges

Coating technology used for oil and gas components includes methods such as chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating, flame spray, sol-gel, and polymer linings. Polymer linings, electroplating and sol-gel can be used for interior coatings, but do not provide dense, hard or low friction-enough films and require a thick coating. A thicker coating occupies more of a pipes internal diameter, which ulti-

mately restricts flow. Of course, plating processes also require the use of harmful chemicals (e.g. hexavalent chrome for hard chrome plating). One difficulty with polymer linings is they can result in a plugged well if the lining adhesion fails. CVD and PVD are low-pressure, plasma-based methods which provide the highest-quality films with regard to purity, adhesion, wear, uniformity, and the least environmental impact, but coating of internal surfaces previously has been limited to small aspect ratios (length / diameter). Both of these techniques require the use of a specialized vacuum chamber, making it difficult to coat large, complex components.

Newer processes entering the market must enable the use of high-quality CVD processes for interior surfaces without the need for a separate vacuum chamber. The resulting coatings must provide protection from wear and corrosion with high hardness, low coefficient of friction (COF) and good adhesion. New processes also must enable the use of much-less expensive base materials, which can then be coated with a thin film that does not constrict flow, but also produces the desired properties.

## Anatomy of an Oil and Gas Industry Pipeline Coating

For piping or tubing that delivers corrosive material, the interior surface that is in contact with the corrosive material is the surface that must be coated. In the case of low-pressure techniques such as PVD, where the pressure is below or near the molecular flow region, coating internal surfaces has been limited to tubing with large diameters and short lengths, due to line of sight deposition. CVD techniques are limited in this application as well, due to the need to supply heat for the chemical reaction, which damages heat-sensitive substrates. Plasma Enhanced Chemical Vapor Deposition (PECVD) can be used to lower the temperature required for reaction, but then there is difficulty in maintaining a uniform plasma inside the pipe and preventing depletion of the source gas as it flows through a pipe placed inside a vacuum chamber.

Various methods of coating the interior surfaces of tubes have been attempted whereby the source material to be coated is inserted into the tube and then sputtered or arced off onto the tube.[2,3] This type of arrangement has several drawbacks including being limited to only large diameter tubes (due to having to insert the cathode tube with associated heat shield and cooling tubes, into the tube to be coated), complicated arrangements for motion of anode and cathode through the tube, and thermal damage to heat-sensitive substrates. New processes for coating pipes are doing so with no need for insertion or movement of the target material (cathodes) through the tube; and there is no excessive heat generated. This is because the part itself is used as a hollow cathode and because a cold, non-thermalized plasma is used.

The material surface properties required for a coating depend on the application and can include properties such as electrical, optical and tribological properties, hardness and corrosion resistance. Sub-One Technology's InnerArmor pipe coating technology enables the deposition of a wide range of films, including metal oxides, metal nitrides and DLC, whose properties can be customized for a given application. Corrosion and wear resistance are the two most critical material characteristics for components used in the oil and gas industries. The type of wear resistance needed can range from rubbing wear of elastomer seals to abrasive or erosive wear from high-velocity sand or mud particles. Corrosive attack is particularly a problem in an environment that prevents or attacks the formation of the protective oxide that forms on stainless steel, such as in a hydrogen sulfide environment common in oil and gas production.

Electrochemical corrosion occurs when the metal being corroded is oxidized and some substance in the environment is reduced. This implies there is a relatively anodic and cathodic area that is coupled to form a galvanic cell. The area of metal attacked is the anode and the area reduced is the cathode.

When a film is used to inhibit corrosion, any pinhole in the film that penetrates to the base metal can act as a site for localized or pitting corrosion, if elements in the film act as a large cathode, with the base metal the anode. Also the grain structure of the film is important, e.g. a columnar structure may promote corrosion due to diffusion through grain boundaries, while a fine grained film will give better results. InnerArmor's amorphous (no grain boundaries), dense, electrically-insulating film structure helps to provide good corrosion resistance.

Several studies have shown that multi-layer films provide improved corrosion resistance.[4,5] A silicon or metal doped DLC base layers provides a superior bond and adhesion to the steel substrate and metal will provide ductility or toughness for applications where this is required such as abrasion and erosion, while the DLC cap provides an inert surface that is highly corrosion resistant and very low friction. Multi-layers also help prevent crack propagation and provide support layers for applications involving abrasion or erosion (**Figure 1**).

Sub-One InnerArmor uses a diamond-like-carbon (DLC) cap layer to coat interior surfaces of pipes and tubes due to its excellent material properties such as high hardness, good corrosion resistance and low coefficient of friction. Properties of DLC films can be tailored by adjusting the $sp^3$ (diamond), $sp^2$ (graphite) and $sp^1$ (linear) bonding hybridization ratios in the film. Amorphous carbon shows no long-range atomic order, as opposed to the long-range order of the crystal structure of diamond. A hydrocarbon precursor such as methane ($CH_4$), acety-

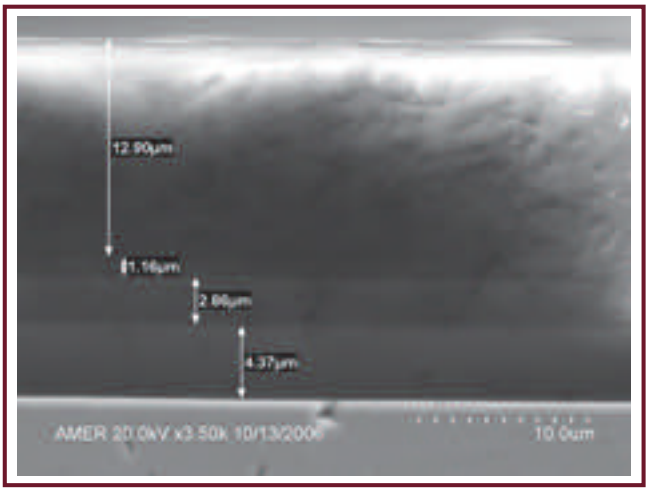



**Figure 1.** SEM of Interior Coating Multi-layer Structure

**Table 1**. Comparison of old and new coating properties.

| Coating Comparison | | | |
|---|---|---|---|
| Coating Name | Company / Process | Hardness (Vickers) | COF |
| | | | |
| InnerArmor™ | Sub-One | 2000 | 0.05 - 0.1 |
| a-C:H | External Coater | 2100 | 0.1 - 0.2 |
| WC 12% CO | Plasma Spray | 1230 | 0.11-0.13 |
| CrO-25%nichrome | Flame Spray | 1200 | >0.3 |
| Hard Chrome | Electroplate | 450 - 1100 | 0.3 - 0.38 |
| Ni-P | Electroless Ni | 1000 | 0.46 |
| Polymer Liner | Epoxy Novolac | 50 | 0.1-0.2 |
| PTFE | | 50 | 0.04 - 0.1 |

lene ($C_2H_2$) or toluene ($C_6H_5CH_3$) is used as the source gas. High $sp^3$ content DLC films have high hardness and high density and take on more 'diamond-like' properties. The "subplantation" model for DLC film formation describes the mechanism for high $sp^3$ bond formation by the insertion of a carbon atom with high enough energy below the surface of the film where it is constrained by the surrounding film, $sp^2$ bonds will be formed at low ion energy on the surface, or at higher ion energy there is a 'thermal spike' resulting in relaxation back to graphite bonding, this leads to an optimum range of ion energy per carbon atom for high $sp^3$ content DLC.[6,7]

Typically high $sp^3$ films have higher compressive stress in addition to higher hardness, which has limited the thickness of these films. Sub-One however has developed methods of depositing high hardness, low stress DLC allowing thicknesses up to 45 mm. Lower stress levels and thicker films can also be obtained by incorporating silicon, nitrogen or other dopants into the DLC matrix.[8] Film properties can thus be tailored by selecting the precursor gas, dopant or bias voltage, or layered films can be deposited. The trade-offs between desired mechanical, electrical or optical film properties and deposition rate and stress for given pre-cursors and bonding hybridizations can be optimized for a given application.[9,10] A comparison of properties for traditional coating techniques and the new interior coating method is shown in **Table 1**.

## New Methods of Deposition

The major challenge for coating internal surfaces is finding new deposition parameters, as both PVD and CVD methods are commonly used on macroscopically flat substrates, such as integrated circuit silicon wafers. Plasma generated externally from a hollow part, will lose ionization as it flows through the part causing poor thickness uniformity. Sub-One's solution to this problem is to use the pipe itself as a PECVD chamber by generating a hollow cathode plasma inside the pipe. As seen in **Figure 2**, this is done by negatively pulse biasing the pipe, which acts as the cathode, with anodes attached at the ends. A gaseous precursor is introduced and ionized causing a coating to be deposited on the pipe, with byproducts pumped out.

A picture of Sub-One InnerArmor's deposition system (**Figure 3**) is shown below. Here the blue anode heads can be seen, that can be easily adjusted to various lengths and diameters of pipes. The process recipe is fully automated and the machine is designed for easy and safe operation and maintenance.Key aspects of Sub-One InnerArmor's process have been developed to meet the requirements of coating internal surfaces, including operating pressure, plasma density, bias voltage, and method of plasma generation. Some of the key concepts of the technology include:

1. The formation of a film from a non-toxic gaseous precursor using low temperature PECVD techniques,
2. The use of the part itself as the vacuum chamber and the generation of a high density hollow cathode plasma within the part,
3. The biasing of the part as the cathode; and
4. The use of DC pulse power.

The use of DC-pulsed power is important for several reasons.

1. DC-pulsed supplies provide higher-peak power, compared to continuously-operated plasmas, while keeping the average power in the usual range.
2. The ability to control the duty cycle (negative bias 'on' time/total period), allows the temperature of heat-sensitive substrates to be controlled.
3. Arcing is eliminated by using bipolar DC pulsing with a low-voltage, short, positive pulse. As a result charge build-up on the film is eliminated.

The excellent thickness uniformity that is generated by the process is shown in **Figure 4**. Here one can see no color transi-

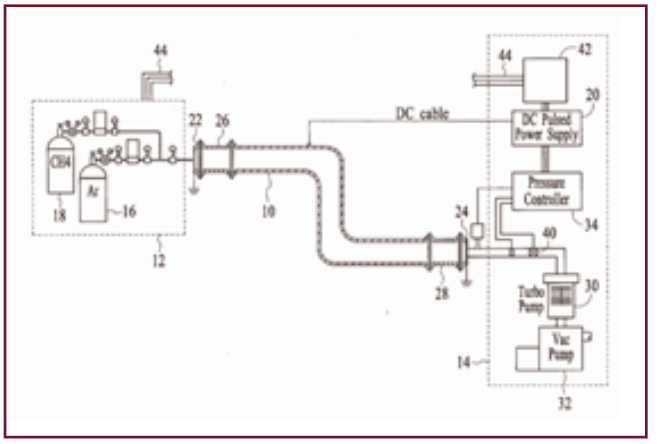



**Figure 2**. Process Set-up [11].

**Figure 3.** Sub-One InnerArmor's deposition system.

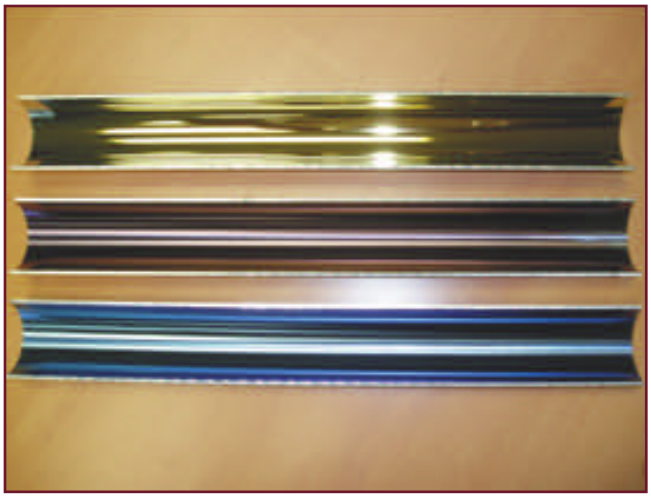


**Figure 4.** Thickness Uniformity.

tion down the length of a 1 foot by 1.375 in diameter pipe, indication a thickness change of <100nm.

Negative bias of the part is done for several reasons including pre-cleaning the surface by sputtering contaminants off prior to deposition; and improving the coating properties with ion-bombardment energy. This results in "activation" of the condensing film, enhancement of surface mobility and denser films, affecting a wide range of mechanical, optical, electrical, and other properties.[12]

Sub-One InnerArmor makes use of a plasma source called the "hollow cathode" that operates at high-plasma densities and high-deposition rates. A hollow cathode is generated by a geometric arrangement, such as a tube or parallel plates, with the tube or plates biased as the cathode. The pressure is adjusted such that the mean free path of the electron is large enough, with respect to the diameter of the part, that electrons accelerated across the cathode plasma sheath at the pipe wall, will reach the opposite wall, causing a pendulum motion of the electron and greater numbers of ionizing collisions.[13] Hollow cathode plasmas will thus have higher plasma densities then similar plasmas under the same conditions. This results in several benefits including a thin conformal plasma sheath and a high deposition rate of up to 1 mm /min. **Figure 5** shows a coupler used in down-hole applications with good coverage of the threading due to the thin, conformal, high-density plasma sheath in conjunction with negative bias.

A wide-range of customer part sizes and aspect ratios have been coated. Currently aspect ratios up to 24:1 can be coated with work on-going for even longer aspect ratios. The ability to coat pipes of this length is of great value to the oil and gas industry that has never been able to coat pipes in this length before using high quality CVD methods.

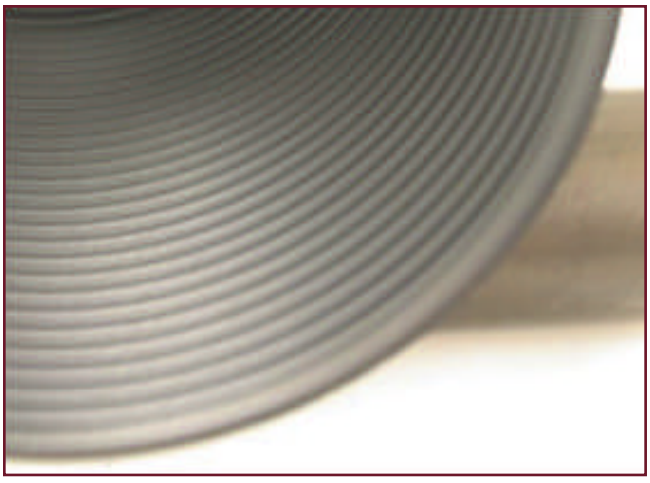


**Figure 5.** Internal Coating of Coupler and Threads.

## Conclusion

As global oil consumption continues, the oil and gas industry will continue to look for new technologies to assist them in the search for the harder-to-reach oil. Sub-One Technology has gained the attention of several of the world's largest oil and gas companies, as well as more than ten major energy service firms. All are attracted to InnerArmor technology based on its ability to coat interior surfaces using PECVD technology providing:

1. High hardness and modulus,
2. Excellent wear and low COF,
3. Corrosion resistance,
4. Safe and environmentally benign chemistry; and
5. Simple and automated coating systems,

The oil and gas industry stands to save billions in corrosion costs and innovation is necessary to do so; advancements in pipe coating technologies could hold the key.

## References


1. (http://www.eia.doe.gov/ emeu/ cabs/topworldtables3_4.html)
2. Wesemeyer et. al., US patent 5026466, (1991)
3. Henshaw, et.al., US patent 4407712, (1983)
4. H.A. Jehn, 'Surface Coatings Tech.', (2000) 131
5. Hovsepian, 'Surface Coatings Tech.', (1999) 120-121
6. Robertson, 'Materials Science & Eng.', R37 (2002) 129-281
7. Bilek, 'Surface Coatings and Tech.', 200 (2006) 4345-4354
8. Donnet, 'Surface Coatings Tech.', (1998)
9. Bhushan, 'Handbook of Tribology', (1997).
10. Corporate web sites.
11. Boardman et. al., US Patent Application, Pub. No. US2006/ 0011468 A1
12. A. Anders, 'Surface & Coating Tech.' (2003)
13. Bardos, 'Non-Conventional Plasma Sources', SVC (2001).