

## QUALIFYING A FOULING REPELLENT THIN SOL-GEL COATING FOR CARBON STEEL SHELL & TUBE HEAT EXCHANGERS

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### ABSTRACT

Sol-gel coatings provide a solution to fouling issues encountered on plate heat exchangers (PHE's) used in crude oil applications. Sol-gel antifouling coatings significantly prolong operation, where otherwise uncoated PHE's require regular maintenance and cleaning procedures to ensure efficient and safe operation. The coatings employed in this study are characterized as being hybrid organic-inorganic 5-10 µm thin repellent coatings with low surface energies. Recently, we have implemented this coating technology on shell and tube (S&T) exchangers and furthermore developed a more inorganic based, fouling repellent, high temperature sol-gel (HTSG) coating for use up to 300 °C/572 °F. The HTSG coating has primarily been verified on stainless steel alloys, as these are employed for S&T exchangers operating at higher temperatures. However, there is also a need for deploying the coating on carbon steel (CS), a frequently used material for S&T exchangers often operating at temperature ranges at which more traditional organic coatings deteriorate.

Here, we present the joint effort by DTI, Curran International and Chevron on qualifying the HTSG coating for application on CS S&T heat exchangers. Development and scale-up of the coating was performed at DTI. The application procedure on inner diameter (ID) of tubes was developed by Curran International and the subsequent validation was carried out by both Chevron and DTI. Results showed that the HTSG coating can be scaled up for industrial application and applied in an adequate layer thickness for commercial S&T heat exchangers.

### INTRODUCTION

Fouling in crude oil heat exchangers is an ongoing challenge for operators, which requires

time-consuming maintenance and cleaning procedures. In some cases, fouling can induce damage mechanisms such as high temperature hydrogen attack (HTHA) or high temperature sulfidation (Jackowski et al. [1]). Without proper cleaning or fouling mitigation, heat exchanger failure can lead to catastrophic incidents as described in the Chemical Safety Board report [2].

Use of repellent sol-gel coatings to mitigate crude oil fouling has been tested on PHE's (Santos et al. [3]; Holberg and Bischoff, [4]) and S&T exchangers (Bischoff et al. [5]). Today, these coatings are commercially available for use on PHEs. The employed sol-gel coatings are made up of a backbone of SiO<sub>2</sub> and has various non-fluoro surface additives which provides the coating with an effective oil repellent effect.

S&T exchanger operational temperature can exceed 200 °C/392 °F, therefore in order to implement the coating technology for these types of S&T exchangers, development of a new sol-gel coating was required as earlier systems would start to deteriorate above 200 °C/392 °F. This resulted in the development of a HTSG coating. In order to operate at higher temperatures, this coating is mostly inorganic in nature. The HTSG coating has earlier been qualified for use on AISI316L stainless steel (Bischoff et al. [6]), as this, and similar grades of stainless steel, is the preferred material for S&T exchangers operating at 300 °C/572 °F or higher. With the successful test and industrial application trials on AISI316L, focus was shifted to test the HTSG coating on CS as this material is often used for S&T exchangers operating at temperatures up to 230 °C/ 446 °F.

Herein we report the work done in order to qualify the HTSG coating for use on CS, with the aim of coating a S&T heat exchanger set for field operations at approximately 230 °C/ 446 °F.

## METHODES

The HTSG coating was applied onto either 1) CS coupons of type LA P265GH cut to size by either a saw or using a pneumatic scissor or 2) the ID of 3/4" CS tubes of type SA 214.

The HTSG coating was applied by either 1) conventional High Volume Low Pressure (HVLP) SATA mini-jet 4 spray gun (size 0.8 mm nozzle) and pressurized air at 2.5 bar or 2) by high pressure atomization for applications inside small ID tubulars. After application, the HTSG coating was allowed a brief 5-minute solvent flash-off before the coating was cured at 90 °C/194 °F for 15 min. and subsequently at 300 °C /572 °F for 3 h.

Coating thickness was measured with a Bykotec 7500 (Byk-Gardener) on flat samples and an elcometer 456 with a 6 cm 90-degree probe on tube ID. SEM/EDX element mapping was utilized to compare with the thickness measurements obtained by the elcometer 456 device.

Adhesion was tested by cross-cut/tape test according to ISO 2409 but with two differences: Tesa Krepp 4331 by Tesa was used as tape and the tape tear-off was repeated three times. The test was rated from 0 (best) to 5 (worst) both after making the cross-cut and after subsequent tape tear off.

Surface energy was measured using a series of polar test inks (Plasmatrete, Series C - Ethanol) with known surface tensions ranging from 30-72 mN/m. The principle of using test inks relies on the observation that a liquid with a lower surface tension than the coating will wet the sample, whereas a liquid with a higher surface tension than the coating will not. Test inks were applied to cleaned samples using a fine brush. If the ink wetted the sample for more than 2 sec, the ink was removed, and the next higher surface energy ink was applied. This process was repeated until the ink beaded within 2 sec of applying the ink. This value is reported as the surface energy by the test ink method.

The thermogravimetric data was obtained from Thermogravimetry Analyzer (TGA, TA 951) performed in air from a temperature range of 25 °C /77 °F to 900 °C/1652 °F with a heating rate of 5 °C/ /41 °F pr. min. Additionally, the thermal stability of the coating was analyzed at 240 °C/464 °F by placing coated CS samples for a defined period of time, in an oven with air circulation.

To evaluate the application trials on tube ID cut sections were tested in crude oil at elevated temperature and pressure in a closed cylindrical test vessel (termed a LOTU, Laboratory Oil Test Unit), to simulate field conditions.

## RESULTS AND DISCUSSION

### Coating Characterization

Applying the HTSG coating by spray coating onto CS coupons yielded a smooth and crack-free

transparent coating after curing. Coating characterization is summarized in Table 1.

Table 1 Adhesion and surface energy data for freshly prepared HTSG coating and after 2 weeks at 240 °C/464 °F

HTSG	Freshly prepared	After 2 weeks at 240 °C
Adhesion	0	0
Surface energy	< 30 mN/m	< 30 mN/m

TGA analysis (air, 5 °C/min) of the HTSG coating showed an onset of main decomposition at 488 °C / 910.4 °F.

### Application trials on tube ID

Initial laboratory screenings demonstrated that the HTSG coating could be applied to CS coupons and, once cured, had good adhesion to the substrate and a low surface energy. Additionally, 2 weeks of exposure to 240 °C/464 °F did not change neither of these properties.

In order to implement the HTSG coating industrial on S&T heat exchangers the coating must be applicable in an adequate DFT layer in industrial settings. For this step, coating was provided for application trials at Curran International with the aim of achieving a sufficient DFT on the ID of 3/4" SA 214 CS tubes. Succeeding application, tube sections were sent to DTI for precise DFT measurements and coating integrity analysis by SEM/EDX element mapping.

The HTSG coating was applied on the tube ID and the top and bottom parts of the tube was marked in order to assess whether, due to coating flow before curing, DFT would be considerable higher at the bottom part compared to the top part of the tube. It was clear from SEM/EDX that the coating filled out the surface roughness and formed a homogeneous layer on the substrate. DFT comparison between top and bottom part is summarized in Table 2.

Table 2 Comparison of DFT between top and bottom part. Measurements done by SEM/EDX.

	Top part	Bottom part
DFT / μm	2-6 (Fig. 1)	3-10 (Fig. 2)

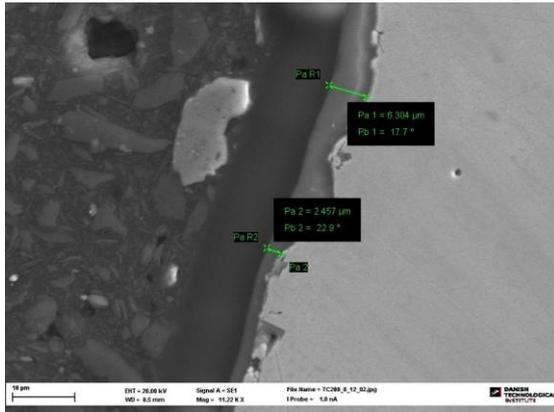


Fig. 1 SEM image from top part of coated tube ID

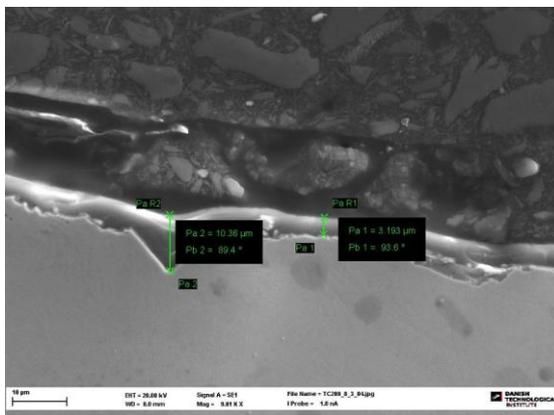


Fig. 2 SEM image from bottom part of coated tube ID

Although there is a slight difference in DFT when comparing the top and bottom part of the tube ID, the top part still has a sufficient layer thickness and the coating is homogeneously distributed across the top part of the tube. This shows that the employed application method sufficiently covered the tube ID with a DFT in the required range and without defects.

In addition, lengths of tubes were cut open to examine the coating. Visually the coating appeared smooth and glossy without defects. Adhesion was measured by the cross-cut/tape method and achieved the best score of 0 (no coating removed). Surface energy was measured to 30 mN/m with test inks. Based on these findings the HTSG coating, when applied on CS tube ID, had the same coating properties as seen when the coating was initially characterized on CS coupons.

#### Exposure of Coated Tube ID to Simulated Field Conditions

Coating trials at Curran International attested it was possible to apply the HTSG in an adequate coating thickness and obtain the same properties regarding DFT, adhesion and surface energy as earlier reported in laboratory trials.

In order to further qualify the application trials, coated ID of CS tubes from the application trials were tested in a specially designed cylindrical test vessel (LOTU) under simulated field conditions. The samples were subjected to 1000 h in crude oil at 240 °C/464 °F and 5-8 bars of pressure. Following the 1000 h exposure test the coated tube sections were evaluated regarding adhesion and surface energy. Cross-cut/tape test showed a perfect adhesion score of 0 (no coating removed) and surface energy was measured to 34 mN/m with test inks. This shows that when the HTSG-coating is exposed to this media in correlation with the increased temperature and pressure it does not influence the HTSG-coatings adhesion to the CS material. The testing conditions only have a slight influence on the surface energy following the prolonged test.

Samples, after the 1000 h exposure, were also analyzed by SEM/EDX. SEM images showed a very uniform coating layer on the CS tube without defects, cracks etc. EDX element mapping showed a distinct layer with a strong Si-signal which correlates to the HTSG coating (Fig. 3).

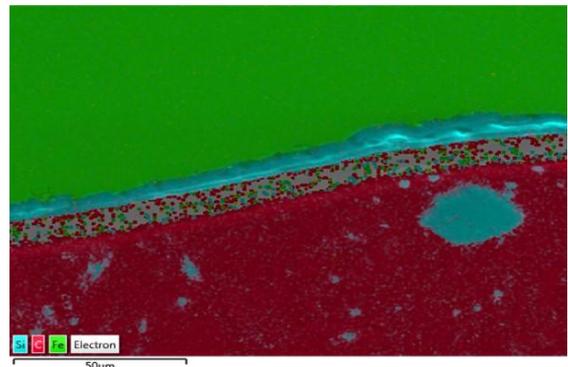


Fig. 3 EDX image of coated tube section after 1000 h exposure in crude oil at 240 °C/464 °F and 5-8 bars of pressure. Green = Fe, cyan = Si, Red = C

From this, DFT was in the range of 2-5 μm which fits well with earlier measurements from coating trials on tube ID.

#### CONCLUSION

In this work it has been demonstrated that the HTSG coating can be applied on CS substrates. Once cured, a smooth and crack free coating is obtained which has excellent adhesion to the substrate as well as a low surface energy.

Furthermore, application of the coating on CS tube ID has been undertaken at an industrial

applicator, with the aim of achieving an adequate DFT on tube ID. Trials showed that it was possible to apply a completely homogenous layer of the HTSG coating on CS tube ID with DFT in the range normally obtained for this coating. When comparing top/bottom parts of the coated tube ID it was found that there was only a slight increase in the DFT at the bottom part of the tube compared to the top part.

Finally, coated tube sections from the application trials were also subjected to simulated field conditions in crude oil at 240 °C / 464 °F and 5-8 bars pressure for 1000 h. At the concluding analysis of these samples the adhesion remained as good as for freshly prepared samples and the surface energy was only slightly increased.

## NOMENCLATURE

### Subscript

CS	Carbon steel
DFT	Dry film thickness
HTHA	High temperature hydrogen attack
HTSG	High temperature sol-gel
HVLP	High volume low pressure
ID	Inner diameter
LOTU	Laboratory Oil Test Unit
PHE	Plate heat exchanger
S&T	Shell and tube
SEM/EDX	Scanning electron microscopy/ Energy-dispersive X-ray spectroscopy
TGA	Thermogravimetric analysis

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