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FOULING-REPELLENT COATING FOR SHELL-AND-TUBE HEAT EXCHANGERS

C. Bischoff[1], T. Poulsen[1], R. Losada[1], J.O. Mortensen[1], L. Jackowski[2] and S.T. Taylor[2]

[1] Danish Technological Institute, Kongsvang Allé 29, 8000 Aarhus C, Denmark, E-mail (Corresponding author): clb@dti.dk
[2] Chevron Energy Technology Company, Richmond, CA, USA

ABSTRACT

Fouling of heat exchangers poses a significant challenge for operators, requiring regular maintenance and cleaning procedures to ensure efficient and safe operation of equipment. Alternative approaches to maintaining clean heat-transfer surfaces that are cost-effective, and do not disrupt equipment availability, are sorely needed by industry. Recent efforts have focused on developing novel surface treatments to mitigate fouling and promote continuous operation of process-critical exchangers without compromising heat transfer efficiency. Thin fouling-resistant coatings for plate-and-frame heat exchangers are beginning to find their way into industrial services, but similar commercial solutions do not exist presently for shell-and-tube (S&T) exchangers.

This document presents results on the tests of a fouling repellant coating technology for use on carbon steel S&T heat exchangers. The applied coatings exhibit outstanding repellency towards a broad range of organic and inorganic fouling species encountered in crude oil processing. We describe application of coatings onto carbon steel materials – the main currency for S&T exchangers in petroleum handling and refining – and test their viability in different process fluid environments. We investigate the fouling performance of these coatings in hydrocarbon and produced water environments and comment on their viability for industrial use in S&T exchangers.

INTRODUCTION

The mitigation of fouling in crude oil heat exchangers relies primarily on hot-runs, chemical treatment and onshore cleaning and refurbishment procedures. Depending on the operational conditions, these procedures may be quite frequent, time consuming and costly. The use of coatings for the mitigation of fouling is known (Santos et. al., 2013) and anti-fouling coated titanium plate heat exchangers for use in crude oil cooling are commercially available. S&T heat exchangers for crude oil processing propose a quite different substrate and operational environment -- the material of choice being carbon steel and the operational conditions often characterized by higher temperatures and pressures than that experienced in plate and frame heat exchangers.

To investigate the use of Sol-Gel derived anti-fouling coatings on carbon steel, variations on pretreatment/priming, coating application and composition were evaluated. Coated carbon steel samples were tested in immersion tests with different media and a range of coating parameters was characterized. For tests at elevated temperatures and pressures, a test vessel has been designed and produced.

METHODS

Coatings were applied onto either 1) carbon steel (CS) coupons of type LA P265GH, cut to size by either a saw or using a pneumatic scissor or 2) tube sections of type EN 10220/10217-2 P235GH TC1 which correlates to ASTM SA214 cut into size with a saw. Prior to treatment the pipe sections were abraded with an abrasive steel wire disc to loosen oxides.

Different surface pretreatments were tested to evaluate their influence on coating adhesion. For the static crude oil test these comprised of 1) *solvent cleaning* by wiping the sample with first acetone and then ethanol, to remove cutting oils and particles, 2) *Planar grinding* with an all round slip maxos grinding stone, to remove the oxide layer in addition to cutting oils and particles, 3) *citric acid* treatment on planar grinded samples. Samples were degreased with acetone followed by alkaline cleaning for 30 min. at RT in 20 % Tickopur TR 33. Samples were then rinsed with demi. water and dried at RT followed by an etching in an aqueous solution of 6 W% citric acid and 4 W% triethanolamine (TEA) for 1 h at 70-80 °C. Following the treatment samples were cleaned in an aqueous solution of 3 W% TEA and finally an aqueous solution of 1 W% TEA is sprayed onto the surface and left to dry at RT. 4) *Bonderite* treatment with Bonderite M-NT 1455T (Henkel) which is a modified Ti phosphate conversion coating. Planar grinded samples were degreased with aceone and ethanol and then alkaline cleaned 30 min at RT in a 20 % solution of tickopur TR 33. Samples were then immersed in a 7 %W aqueous solution of the Bonderite solution for 20 sec. at RT before being dried 30 min at 60 °C. For the dynamic test in crude oil:water (1:1 W%) mixture planar grinding was not employed. Instead two additional pretreatments were tested: 1) *Cold-Phos* treatment with Cold Phos/ARO (Vecom) which is an iron phosphate coating. A 1:2 volume solution af cold-Phos and demi. water is sprayed onto the tube which is then dried 6 h at RT. 2) *2K epoxy primer* with MIPA-EP100-20-2K-EP-Grund. The primer, due to a high viscousity, was applied by brush.

Table 1. Curing Conditions for the Four Selected Sol-Gel Coatings.

Type of Coating	Curing Temp. °C	Curing Time h
Coating 1	200	1
Coating 2	185	1
Coating 3	140	1.5
Coating 4	140	0.5

Four different repellent sol-gel coatings were tested. These are hybrid (inorganic-organic) sol-gel coatings obtaining their repellency from polydimethylsiloxane (PDMS). See Holberg and Bischoff, 2014 for further coating background. All coatings were applied by conventional air spray using a SATA mini-jet 4 High Volume Low Pressure (HVLP) spray gun equipped with a size 0.8 nozzle and pressurized air at 2.5 bar. Following application the coatings were cured according to table 1.

Coating thickness was measured on nine spots per sample with a Bykotest 7500 by Byk-Gardener.

Coating adhesion was tested by both cross-cut and 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 at each stage. The test was rated both after cross-cut and after subsequent tape tear-off.
Ferricyanide spot test is done by applying drops of a slightly acidic 10 % aqueous solution of potassium ferricyanide. The drops are left for 1.5 min. on the coated surface before being removed. Blue spots in the drops indicates free Fe^{2+} which arises from part of the CS not being covered by the coating.

RESULTS AND DISCUSSION

Static Crude Oil Test

For initial evaluation of the coatings durability upon crude oil expositor, coated CS coupons were submerged in crude oil for a month. The four different sol-gel coatings (Coating 1-4) were applied by spraying on CS coupons with four different surface treatments eg. solvent cleaning, planar grinding, citric acid treatment and Bonderite treatment. All four sol-gel coatings showed perfect wetting on CS with the four different surface treatments. Coating adhesion was evaluated by cross-cut and tape test. None of the coatings displayed reduced adhesion except Coatings 3 and 4 on solvent cleaned and planar grinding samples. These samples were discontinued for immersion test. Ferricyanide tests conducted on the remaining samples showed either no blue spots or very small discontinuities which were regarded as insignificant due to the very small number and size of the spots. This indicates the coating is free of defects. The coating thickness of the samples were in the range of 2.5 to 13.6 µm.

Coated CS coupons (duplicates) with cross cut were submerged in crude oil at RT. The performance of the coatings was evaluated by assessing the repellent effect when samples were removed from the oil, visual inspection of the coating to determine signs of blisters, creeping or corrosion and testing coating adhesion.

The criteria used to determine the most promising combination of pretreatment and coating was based on the following points ranging from most to less important: 1) no adhesive failure, 2) lowest amount of corroded areas underneath the coating, discontinuities of the coating and/or areas with blisters or other coating defects, 3) strong oil repellency. Based on these criteria the following was observed:

- Best results were obtained with Coating 3 and 4 when applying a pretreatment (citric acid or Bonderite) and Coating 1 with and without pretreatment as these showed excellent adhesion and no signs of corrosion. The coatings showed good oil repellency.
- Coating 2 also performed very well with or without pre-treatment, showed excellent adhesion and no signs of corrosion. Repellency was slightly reduced for the Bonderite samples but otherwise repellency was good.

Dynamic Test in Crude Oil:Water (1:1 Wt%) Mixture

To better simulate real test conditions a new immersion set-up was utilized. This set-up differs from the static test in the following regards: 1) the test is conducted in a 1:1 weight% mixture of crude oil and demineralized (demi) water. This composition was chosen as typically there will be water present in the crude oil passing through a S&T exchanger; 2) the test is dynamic, which means the crude oil:water mixture is continuously stirred throughout the test. This was done to simulate the movement of crude oil though S&T pipes; and 3) coatings were applied on the outside of CS tube sections.

The four selected sol-gel coatings (Coatings 1-4) were applied by spraying on five different surface treatments eg. solvent cleaning, citric acid, Bonderite, Cold-Phos and 2K epoxy primer. All four sol-gel coatings showed perfect wetting on CS tubes with the five different surface treatments. Cross-cuts were made for all samples and adhesion evaluated by tape test. None of the coatings displayed reduced adhesion. It is interesting to note that Coatings 3 and 4, which previously failed the adhesion test on solvent cleaned CS coupons, show no reduction of adhesion when applied to CS tubes. It is believed to be due to the difference in pretreatment. The coupons were planar grinded which leaves a very smooth surface whereas the tubes were abraded with a steel wire disc which leaves the surface more rough. A rough surface is more favorable for obtaining better coating adhesion which explains why Coatings 3 and 4 show no reduction of adhesion on the CS tubes.

Figure 1 depicts a coated CS tube immediately after extraction from the 1:1 crude oil:water test media. The oleophobic/hydrophobic properties are intact, as evident by the immediate drainage of liquids from the coated metal surface.

Figure 1: Following extraction from the crude oil:water test media, the liquids drain immediately from the coated tubes (right). The liquids remain on an uncoated tube section.

Following 6 months of continuous immersion, a number of samples were still showing excellent performance. The criteria used to determine the samples displaying the most promise were based on the following points ranging from most to less important: 1) no adhesive failure, 2) lowest amount of corroded areas underneath the coating, discontinuities of the coating and/or areas with blisters or other coating defects, 3) strong oil repellency. Based on these criteria the following were observed:

- The best performing candidate is Coating 2 with the citric acid, Bonderite and Cold-Phos treatment. The samples showed excellent adhesion and no signs of corrosion. Oil repellency was deemed to be the strongest among the four tested sol-gel coatings.
- Coating 1 with citric acid, Bonderite and Cold-Phos show excellent adhesion and no sign of corrosion. Oil repellency is less pronounced when comparing to Coating 2 and 3.
- Coating 3 with citric acid, Bonderite and 2k epoxy primer all show excellent adhesion and no significant signs of corrosion. On some samples, there are areas underneath the coating, which could be associated with corrosion processes but they do not affect either repellency or adhesion. Oil repellency was less pronounced compared to Coating 2 but better when compared to Coating 1.
- Coating 4 with citric acid and Bonderite show excellent adhesion and no significant signs of corrosion. However, when removing the samples from the crude oil:water mixture the coating did not show repellency.

Hydrolysis Stability Test

To gain better insight into the performance of Coating 2 in pure water, a similar test as the one detailed for the crude oil:water test was set-up with demineralized water as the medium. Pipe sections were coated with Coating 2 and pretreatments of citric acid, Bonderite and Cold-Phos were used. Cross-cuts were made in the coatings and the samples were submerged in demi water at 70 °C. Following 72 h, the pipes were removed and evaluated regarding adhesion and coating defects. Results are listed in Table 2.

Table 2. Observations and Adhesion of Coating 2 with Different Pretreatments Following 72 h of Immersion in 70 °C Demi Water.

Sample	Observation	Tape test
No treatment	Large number of black spots, rust on cross cut	2
Citric acid	Black spots mostly concentrated in two areas of the sample. Rust on cross cut	1
Bonderite	No black spots or other defects. Rust on cross cut	0-1
Cold-Phos	Small pit on the surface, otherwise no defects	0-1

Further tests

To evaluate the performance of the coatings at elevated temperatures, a test vessel, which can be charged with crude oil for exposure to elevated temperatures and pressures, has been designed and constructed. The vessel, coined LOTU for Laboratory Oil Test Unit, is essentially a ‘bomb’ where a set of four coated test coupons, can be subjected to a temperature of up to 320 °C and a pressure of up to +100 bar. Initial tests with the unit have been performed, and demonstrate the of the unit as well as service viability of the coatings. For the coming work, the unit will be used to test coated CS samples in crude oil contact at 300 °C and 35 bar.

Future work will also evaluate fouling performance of different coating formulations on carbon steel tubing in crude oil and produced water under simulated heat exchanger conditions. These tests will afford more quantitative measures of fouling mitigation compared to bare metallurgy, and will help to guide further performance improvements.

CONCLUSIONS

Coating of carbon steel shell and tube heat exchangers presents several interesting coating technological challenges. The substrate is not trivial to coat and the operational circumstances in a S&T unit is often characterized by high temperature and pressure, which further challenges a coating. We have here presented the initial coating developments and tests required to demonstrate a coating technology that may be employed on such substrate under such circumstances.

The coating technology, that is successfully employed on titanium plate and frame heat exchangers, has demonstrated excellent stability and repellent properties in crude oil coolers (Santos et. al., 2013, Holberg and Bischoff, 2014). A series of derived coatings have been tested on carbon steel, using different pretreatments, and exposing the coating to different test media. In the ongoing tests, coating 2 applied on a cold phosphate treated carbon steel surface has the most promising characteristics. Work is continuing on further documenting the coatings, especially in crude oil contact at relevant temperatures. Obtaining a S&T exchanger coating technology, capable of repelling crude oil fouling components as effectively as has been demonstrated on titanium plate and frame heat exchangers, will potentially reduce the S&T exchanger service requirements dramatically and offers great potential for cost savings and reduced environmental load.

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