PIGMENTED ANTIFOULING COATINGS FOR IMPROVED ON-SITE INSPECTION

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ABSTRACT

Sol-gel derived antifouling coatings for use in crude oil processing heat exchangers have been successfully utilized for years. The combination of a very thin and heat conductive coating with low surface energy and low surface roughness in an inert glass ceramic matrix has proven very effective in preventing fouling accumulation and maintaining sustained production. It has been documented that the operation of both plate heat exchangers (PHEs) and shell and tube (S&T) heat exchangers can be extended dramatically. From only weeks or months of operation of uncoated units to several years of operation of coated units - without the need of time consuming and costly service procedures.

A challenge using very thin and transparent sol-gel coatings is reassuring that the items are actually coated and are correctly applied. For PHEs, that may only be single side coated, it is important that the unit is assembled correctly, so that the coated side of the heat exchanger plates face the crude oil. Also, for inspection purposes and for estimation of residual lifetime, it is important to be able to establish the quality of the coating efficiently and quickly – also inside the individual tubes of a S&T exchanger.

Here we present ongoing coating development work of TC200, an antifouling coating stable up to 300 °C/572 °F of operation, which is provided with inert and heat stable pigments that allow quick inspection of coating integrity, both before and after operation. Together with procedures for testing coating repellency and substrate adhesion, the pigmented TC200 coating may facilitate the industrial transition to antifouling coatings.

INTRODUCTION

Fouling in heat exchangers that process crude oil cause costly and time-consuming consequences (Jackowski et al. [1]). Coatings that reduce formation of fouling on heat exchanger surfaces in contact with crude oil have been intensely researched and also commercially used for many years. Among the coating technologies employed to improve operation under crude oil derived fouling conditions is sol-gel technology. Both for plate heat exchangers (Santos et al. [2]) (Holberg and Bischoff [3]) and shell and tube heat exchangers (Bischoff et al. [4]). Sol-gel derived coatings, typically hybrids based on silane compounds, are often thin, transparent and robust. Very smooth, inert and provided with low surface energy surfactants, sol-gel coatings have proven very effective in prolonging the operation of different crude oil processing heat exchangers. Operation can often be extended severalfold without need for service. From a heat exchange point of view, the thin, glass ceramic like nature of the sol-gel coatings is optimal, as it only causes a minimal impact on the heat conductivity of the system.

However, the coatings being thin and transparent also provide a challenge: As the coatings are practically invisible, it can be very difficult to identify a coated surface or to tell the status of a coated surface on a piece of equipment that is taken out of service. There are practical solutions to this, which may include the use of coating thickness gauges or surface energy test inks. But such solutions are often impractical for on-site use. It is therefore relevant to develop a colored anti-fouling sol-gel coating that allow quick identification of coated surfaces and that also provides an easy way to tell the status of coated equipment that have been in prolonged use.

Herein, we report the work and laboratory trials done in order to modify and test a version of Thermo Coat 200 (Poulsen et al. [5], Bischoff et al. [6]) with pigments that allow easy on-site inspection.

METHODS

Coatings

The starting point for this work was Thermo Coat 200 (TC200) which have been described elsewhere (HTSG in Poulsen et al [5], Bischoff et al [6]). TC200 is a thin, transparent sol-gel coating that forms a smooth, crack free coating with excellent substrate adhesion, low surface energy and good antifouling properties.

For obtaining a colored coating, both the use of chemical dyes and pigments were explored. Use of chemical dyes present two drawbacks, that lead to the disqualification of this approach. One being that the very thin and glass like nature of the coatings, makes it very hard to obtain a sufficiently intense dye signal to ensure positive identification of the coating and its integrity. The second being that the high operational temperature, up to 350 °C, required for the coating, disqualified the use of the identified dyes. With focus on pigments, titanium dioxide (TiO_2) particles were selected. TiO_2 is an often-used pigment in the coating industry and is attractive for this application due to very good thermal stability, it provides a bright white color, it is available in bulk quantities and is not too costly. Compared to dyes, a challenge presented by the use of pigments in the thin and smooth sol-gel coatings, is that the pigments may cause a roughening of the surface, that may be disadvantageous for the fouling repellent properties. To ensure minimal impact on roughness, a nano scale titanium dioxide pigment was used.

TC200 variants containing 3, 4, 5 and 10% titanium dioxide were formulated and tested. To ensure good dispersion of the particles in the coating material, prior to application the coating was ultra sonicated using a Hielscher UP200H Ultrasonic Processor equipped with a Ø 10 mm sonotrode and set at 0.8 cycle, 80% amplitude for 2 x 1 minute.

Substrates

AISI316 coupons were used for the initial coating modification trials. Coated AISI 316 coupons, size 76 x 152 mm, were subjected to a range of relevant laboratory trials as described below (application tests, adhesion tests, cross cut tests, thermal stability tests, surface roughness analysis, hydrolysis stability trials). AISI316 tubes (Ø 18 mm, ID 16 mm, 500 mm length) were used for tube application trials.

For flat coupons application was performed with a standard High Volume Low Pressure (HVLP) spray gun (SATA mini-jet 4, nozzle size 0.8 mm). For tube application, a 100 cm lance equipped with a 360° spray fan nozzle was used. After application coated samples underwent a 5 min solvent flash-off before thermal curing, (15 min @ 90 °C/194 °F followed by 3hr @ 300 °C/572 °F).

Before application, the AISI316 substrates were cleaned with solvent and primed with DTI-7. Coating thickness was measured by a BYK Gardner Byko-test 7500 thickness gauge.

RESULTS AND DISCUSSION

Flat coupons were coated as described with four variants of TC200 containing 3, 4, 5 and 10% w/w TiO_2 relative to the total wet coating mass. All four variants give rise to coatings with good wetting properties and good wet film formation. Following curing, all four formulations give rise to homogenous, white coatings that are easily recognizable compared to the conventional TC200 without added pigments. Coating thickness was measured to approximately 8-10 µm. Figure 1 show the clear visual difference between TC200 without pigments and TC200 with 5% TiO_2 added.

Figure 1: Left coupon: TC200 without added pigments. Right coupon: TC200 with 5% TiO_2

Cross cut tests

To investigate whether the addition of TiO_2 impacts adhesion, cross-cut/tape test was conducted according to ISO 2409 using Tesa Krepp 4331 from Tesa. The coatings were rated from 0 (best) to 5 (worst). Results are presented in table 1.

Table 1: Cross cut scores of TC200 with different amounts of added TiO_2

Coating	Adhesion score
TC200	0
TC200 + 3% TiO_2	0
TC200 + 4% TiO_2	0-1
TC200 + 5% TiO_2	0-1
TC200 + 10% TiO_2	3-4

The addition of TiO_2 does impact adhesion of the coating especially at higher concentrations. At 3% the added TiO_2 does not appear to have an impact that is measurable in this test. However, at increasing concentrations of TiO_2, there appears to be a gradual degradation of the adhesion. Based the cross cut trials, it was decided to discard further trials with TC200 + 10% TiO_2.

Surface roughness

The surface roughness of the coatings was investigated using a Mitutoyo SJ-210 profilometer. For each coating system, five measurements were taken, and the average presented in table 2.

Table 2. Profilometry results of TC200 with different amounts of TiO_2

Coating	Average roughness (Ra) [µm]	Standard deviation
TC200	0,06	0,01
TC200 + 3% TiO_2	0,24	0,03
TC200 + 4% TiO_2	0,30	0,03
TC200 + 5% TiO_2	0,33	0,05

In figure 2 a linear correlation between TiO_2 content and surface roughness is evident. This indicates good dispersion of the particles, as insufficient dispersion very likely would permit agglomerates in the coating, which would give rise to a more erratic surface roughness profile.

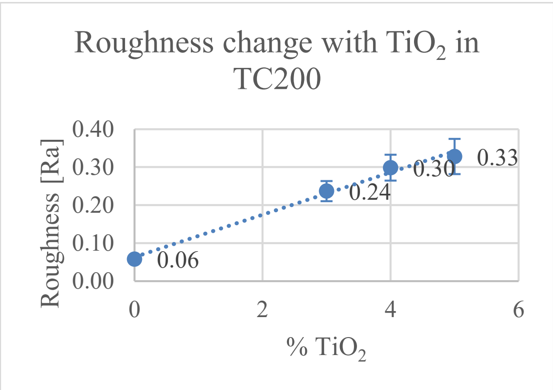

Figure 2: Surface roughness, Ra [µm] as function of TiO_2 content.

Thermal Stability Test

Coated samples were exposed to seven days of 350 °C without visual changes to the coating and without impact on adhesion or changes to the surface energy.

Hydrolysis Stability Test

TC200 show excellent stability in hydrolysis stability tests. To investigate whether the addition of TiO_2 particles to the coating formulation impacts the stability towards hydrolysis, tests were conducted as follows: DTI-7 primed and TC200 + TiO_2 coated AISI316 coupons were subjected to cross cut test and then fully submerged in demineralized water with 3% NaCl. Sample containers were sealed and placed at 90 °C. Following 72 hr. exposure, the samples were removed and evaluated regarding adhesion and coating defects. The results are listed in table 3.

Table 3: Adhesion scores following hydrolysis stability tests

Coating	Adhesion score after exposure
TC200	0
TC200 + 3% TiO_2	0
TC200 + 4% TiO_2	0-1
TC200 + 5% TiO_2	0-1

Surface energy

To examine whether the TiO_2 inclusion impacts the surface energy of the coating, surface energy was determine using a series of polar test inks (Plasmatreat, Series C- ethanol) with known surface tensions ranging from 30 to 72 mN/m. Test inks with a lower surface tension than the surface energy of the tested coating will wet the surface and form a liquid film, whereas test inks with a higher surface tension than the surface energy of the tested coating will not wet the surface and instead form discrete droplets on the surface. Beginning with the test ink with the lowest surface tension, the ink was applied to the surface using a brush and evaluated following two seconds. If wetting was observed the next higher surface tension ink was applied. This process was repeated until beading was observed two seconds after applying the ink. This value was reported as the surface energy by the test in method. Results are presented in table 4.

Table 4: Surface energy as determined by test ink analysis

Coating	Surface energy (mN/m)
TC200	<30
TC200 + 3% TiO_2	<30
TC200 + 4% TiO_2	30-32
TC200 + 5% TiO_2	30-32

Further tests

To obtain more performance characteristics on TC200 with different amounts of TiO_2 added, further tests will be conducted. Two important qualification trials remain, namely 1) Exposure to high temperature crude oil. These tests will be conducted in our LOTU (Laboratory Oil Test Unit), where coated coupons and tube sections can be exposed to crude oil at defined temperature and pressure for an extended period of time. Following the LOTU trials, the coated samples will be evaluated in SEM and relevant parameters, such as substrate adhesion and surface energy, will be evaluated. 2) Fouling tests. The further qualification trials will also include fouling tests of the different coating formulations, where coated samples are exposed to conditions that favor fouling accumulation.

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CONCLUSION

In this work, it has been demonstrated that the sol-gel derived TC200 crude oil fouling repellent coating system can be provided with color through the inclusion of titanium dioxide particles. The color permits easy visual identification of coated surfaces, without impacting coating adhesion, coating thermal stability, coating hydrolysis stability and with only minimal impact on surface roughness and surface energy. Further tests are planned to investigate whether the inclusion of titanium dioxide has influence on fouling repellent properties and stability in high temperature crude oil contact.

NOMENCLATURE

DFT: Dry film thickness
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 heat exchanger
SEM: Scanning Electron Microscope
TC200: Thermo Coat 200

REFERENCES

[1] Jackowski, L., Risse, P. and Smith, R., Impact on nonuniform fouling on operating temperatures in heat exchanger networks, *Heat Transfer Engineering*, 38 (7-8), pp. 753-761, 2016

[2] Santos, O., Anehamre, J., Wictor, C., Tornqvist, A. and Nilsson, M., Minimizing Crude Oil Fouling by Modifying the Surface of Heat Exchangers with a Flexible Creamic Coating. *Heat Exchanger Fouling and Cleaning X*, Budapest, 2013.

[3] Holberg, S. and Bischoff, C., Application of a repellent urea-siloxane hybrid coating in the oil industry. *Progress in Organic Coatings*, 77(19), pp 1591-1595, 2014.

[4] Bischoff, C., Poulsen, T., Losada, R., Mortensen, J.O., Jackowski, L. and Taylor, S.T., Fouling-Repellent Coating for Shell-and-Tube Heat Exchangers. *Heat Exchanger Fouling & Cleaning XI*, Dublin, 2015.

[5] Poulsen, T, Losada, R, Bischoff, C, Curran, E, Jackowski, L., Taylor, S. and Chaloner-Gill, B.,Qualifying a fouling repellent thin sol-gel coating for carbon Steel Shell & tuve heat exchangers, *Heat Exchanger Fouling & Cleaning XIII*, Warsaw, 2019.

[6] Bischoff, C., Losada, R., Poulsen, T., Jackowski, L. and Taylor, S., Development of Thin Sol-Gel Coatings for Heat Exchanger Foluing Mitigation at Elevated Temperatures. *Heat Exchanger Fouling & Cleaning XII*, Madrid, 2017.