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MINIMIZING CRUDE OIL FOULING BY MODIFYING THE SURFACE OF HEAT EXCHANGERS WITH A FLEXIBLE CERAMIC COATING

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ABSTRACT

An oil repellent organic inorganic hybrid coating was applied on titanium plate heat exchanger plates and field tested in an offshore crude oil cooler. The first trial consisted in a partially coated plate heat exchanger (PHE) where after, due to promising results, a fully coated unit was installed. After several months in operation the coated plates were inspected both visually and by the help of a light optical microscope. The following parameters were assessed: Fouling amount and strength of adhesion to the plate, coating condition and repellency. The coating was found to be successful in minimizing the amount of fouling and reducing its adhesion to the plate, where the fouled plate could be completely cleaned by a high pressure water jet, thereby avoiding the use of cleaning chemicals. Only minor areas of the coating presented defects and in major parts of the plate the coating repellency was still intact.

As opposed to the need of sending the plate heat exchanger onshore for reconditioning once or twice a year, depending on the season, the fully coated unit maintained its thermal performance for around 2 years. This implies a huge benefit for the end user not only in terms of increased process efficiency but also lower cleaning related costs (time, energy and chemicals).

INTRODUCTION

Fouling of heat exchangers in the oil industry results in a loss of performance which leads to production stops for cleaning and therefore increased operation costs (Deshannavar, et al., 2010). Crude oil dehydration process consists of produced water being removed from the wet crude oil by a series of separators where the heat transfer between the media is carried out by plate heat exchangers. One of these heat exchangers, the crude oil cooler, cools down the crude oil to the required level by circulating sea water in the adjacent channel. The crude oil will then be stored and transported. The cooling is necessary to minimize evaporation of light hydrocarbons that would otherwise create an explosive atmosphere in tanks. Fouling occurs due to the fact that the temperature at and near the wall in the oil channel can be lower than the wax appearance temperature (WAT) leading to paraffin wax crystallization at the plate wall of the heat exchanger. The WAT depends on the crude oil composition and also on the determination method. Elsharkawy et al. (2000) used differential scanning calorimetry to determine the WAT for different crude oils and reported values ranging from 32 to 38°C. The composition of the wax deposit is time dependent starting with a porous structure which gradually becomes denser as more wax molecules diffuses into the porous structure and oil diffuses out (Singh et al., 2000). The denser the deposit layer the higher the impairment on the heat transfer due to the insulating effect of the wax layer (thermal conductivity of 0.073 W / m K, Torresola, 1998) at the surface and the more challenging the cleaning becomes. Several approaches to mitigate oil fouling are reported in the literature including heating, chemical treatment (inhibitors), paraffin hydrodynamics and surface treatment (Merino-Garcia and Correra, 2008; Paso et al., 2009). In this work we follow the later approach i.e. alteration of the surface properties of the metal substrate.

A literature search regarding the use of coatings for fouling reduction in crude oil cooling plate heat exchangers was unfruitful. Some coatings have however been tested in crude oil. Fernandez and Rothan (2009) compared the performance of coated and uncoated shell and tube reboilers. The coating, a phenolic epoxy polymer, was applied on the tube side where the crude oil flows and was heated with steam on the shell side. No fouling reduction was achieved on the coated reboilers and the coating diminished the heat transfer due to its low thermal conductivity. The effect of different coatings on paraffin wax fouling of cold steel surfaces have also been investigated (Johnsen et al., 2009). Three coatings (no details were reported on two of the coatings while the third consisted of an organic inorganic hybrid coating based on aminopropylsilane) were tested in a batch baffle stirred reactor with a binary test fluid consisting of a paraffinic solvent (n-decane) and paraffin wax solute (n-tetracosane) at different flow velocities. Two of the coatings reduced the amount of wax deposit independent of the flow velocity. Several fouling reducing coatings (SiF_3^+ and MoS_2^{2+} ion implantation, Diamond-like Carbon (DLC) sputtering, DLC-Si-O and SiOx Plasma Enhanced Chemical Vapour Deposition (PECVD), autocatalytic Ni-P-PTFE and silica) have been applied to stainless steel and its surface properties characterized (Santos et al., 2004). Some of these coatings were then tested both at laboratory (Santos et al., 2006) and pilot scale heat exchangers used in the food industry (Rosmaninho et al., 2006; Balasubramanian and Puri, 2009; Patel et al., 2013; Barish and Goddard, 2013). While some improvements in fouling and cleaning were observed for some of the coatings, there is still, to the author's knowledge, no commercially available coated plate heat exchanger. This is due to the complexity of both the fouling mechanism and the coating properties. Besides being able to reduce foulant adhesion a coating, to be suitable to use in a heat exchanger, needs to have a decent thermal conductivity, good wear and abrasion resistance, good temperature and chemical resistance and a good adhesion to the metal substrate.

In this full-scale industrial case study, an organic inorganic hybrid coating has been field tested in a crude oil rig with promising results. The coating was applied on heat exchanger plates and the coated plates assembled on a M20-MFD unit. The duty was cooling of crude oil from 70 to 40 °C using sea water as a cooling media. The duty is highly fouling with wax solidifying on the plate wall together with crystalline substances. The operating time of an uncoated heat exchanger varies between 6 to 9 months depending on the season where thereafter the increase in the pressure drop to unacceptable values together with the inability to cool the crude oil to the required temperature requires the heat exchanger to be open and the plate pack send for reconditioning. During the operating time the heat exchanger is cleaned bimonthly by the so-called hot runs (heating up the oil side by shutting off the cooling water flow resulting in wax being partially dissolved).

EXPERIMENTAL

Coated Surfaces

The oil repellent organic inorganic hybrid coating (ORC) used in the field test was manufactured and applied by an external company. The synthesis of the coating is schematically presented in Fig. 1.

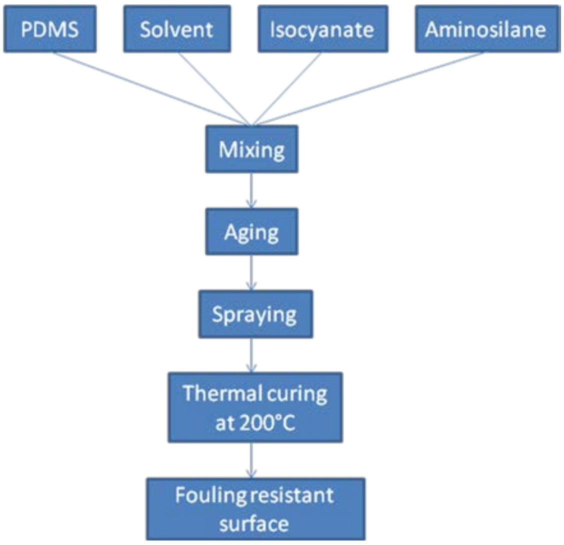

Fig. 1 Diagram of the synthesis of the repellent flexible ceramic coating.

The properties of the coating relative to the reference titanium surface are presented in Table 1 and 2, where the contact angle and surface energy values were provided by the coating manufacturer. The arithmetic mean surface roughness (Ra) was measured by a Perthometer Perthen M4P profilometer on 10 different locations. The sampling points were ridges on the heat transfer surface and the measuring length 4.8 mm (Fig. 2). The coating thickness varies from 5-10 µm as can be seen in a cross-section of a representative coated plate imaged with a scanning electron microscope (Inspect S50) (Fig. 3).

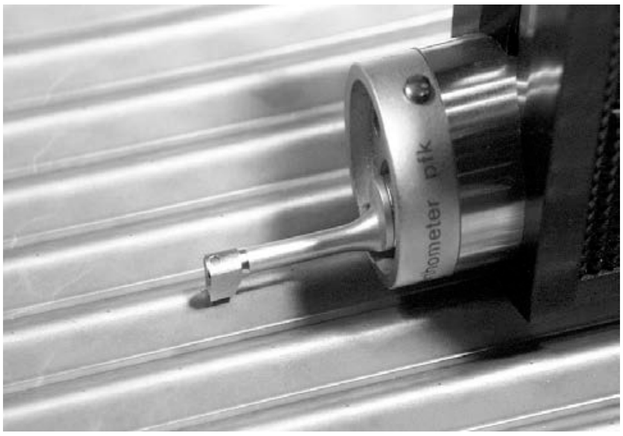

Fig. 2 Roughness measurement with a Perthometer at the ridges on the heat transfer area.

Table 1. Surface properties of the reference and coated substrates.

Surface	Water contact angle (˚)	Formide contact angle (˚)	α-Bromonaphthalene	Surface roughness (µm)
Titanium	80 (4s) 40 (180 s)[a]	60 ± 1	36 ± 2	1,03 ± 0,04
ORC	105 ± 1	92 ± 1	66 ± 2	0,52 ± 0,14

[a] Two time dependent angles are provided since the contact angle is not static.

Table 2. Surface energy of the reference and coated substrates.

Surface	Time	γ^{TOT} (mN/m)	γ^{LW} (mN/m)	γ^{+} (mN/m)	γ^{-} (mN/m)
Titanium	4 s	39	36	0.2	5.8
	180 s	47	36	1.4	20
ORC	static	21	21	0	1.2

γ^{TOT} Total surface energy
γ^{LW} Lifshitz-van der Waals component of the surface energy
γ^{+} acid component of the surface energy
γ^{-} base component of the surface energy

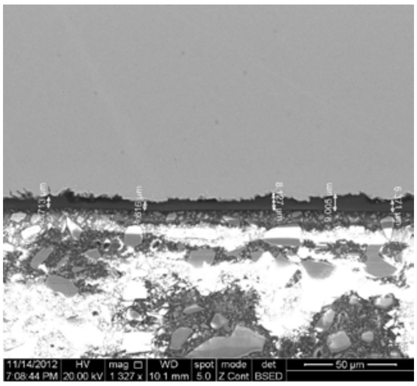

Fig. 3 SEM image of a cross section of a coated plate.

Full-Scale Industrial Field Test

Partially coated plate pack. The first field test was run with a partially coated plate pack in a M20-MFD plate heat exchanger. From the total 349 titanium plates 15 were coated and 5 each placed in the beginning, middle and end of the plate pack (Fig. 4). The unit was in operation for 8 months with hot runs being the only cleaning performed.

The amount of fouling on the coated plates compared to the uncoated reference plates was assessed visually and by weighting the plates before and after the field test. Fouling adhesion was roughly estimated by removal the fouling with a cloth and by high pressure water jet.

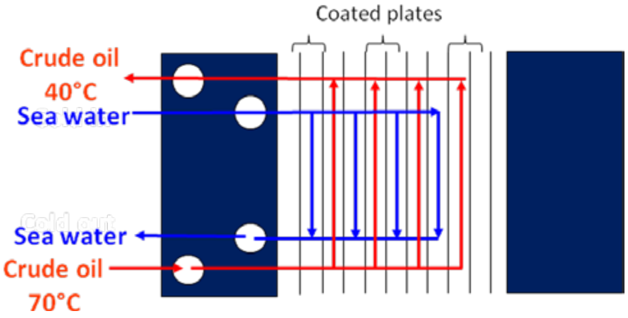

Fig. 4 – Schematic picture of a plate heat exchanger showing the locations of the coated plates.

Fully coated plate pack. The next step was to field test two PHE’s consisting of a fully coated plate pack. One of the heat exchangers was in operation for 5 months before being disassembled and the coating performance investigated. The second heat exchanger was in operation for 2 years.

The coating condition was assessed by visual inspection and with the aid of a LOM. Cross sections of different areas of the plate (distribution area and heat transfer area) were prepared to measure the coating thickness. The coating repellent properties were investigated by the permanent marker test and the fouling adhesion to the coating by cleaning with a cloth and high pressure water jet.

RESULTS

Partially Coated Plate Pack

The coated plates had a lower amount of fouling, a reduction of 65% was determined (Table 3, Fig. 5). The growth of the wax layer was found to depend on the substrate. The uncoated titanium surfaces were covered with a homogeneous layer whereas on the coated surfaces only small islands of wax were seen. Adhesion of the wax layer to the surface was also significantly reduced compared to the uncoated plates, where it was possible to clean the coated plates only with high pressure water jet.

Table 3. Amount of fouling determined on both the titanium and coated plate. The amount of fouling was determined from 5 plates placed at the end of the plate pack. sd standard deviation

Surface	**Average fouling (g) ± sd**	**Fouling reduction (%)**
Titanium	585 ± 125	-
ORC	203 ± 48	65

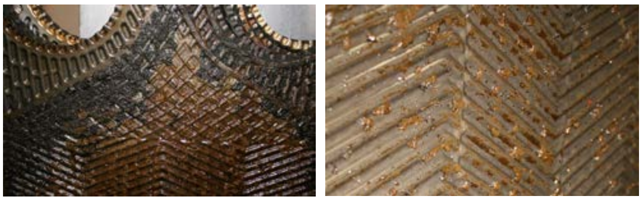

Fig. 5 – Fouling appearance on the reference titanium plate (left) and on the ORC plate (right).

Fouling was also observed to depend on the relative position of the coated plates in the PHE, where less fouling was seen on the plates positioned in the beginning. This can be related to a slightly higher flow rate in this position of the heat exchanger. Minor coating defects and a reduction in coating adhesion were observed after 8 months operation. However, the coating still showed an intact oleophobicity.

Fully Coated Plate Pack

Fig. 6 shows that the amount of fouling on the coated plates was minimal and, as observed on the partially coated plate pack, the wax deposited as dispersed islands. The adhesion of the fouling layer to the plates was very weak where after cleaning with a dry cloth almost no fouling remained (Fig. 7).

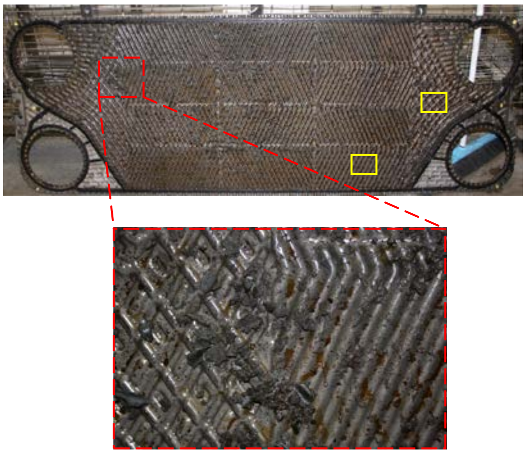

Fig. 6 – Amount and appearance of the fouling on a coated plate.

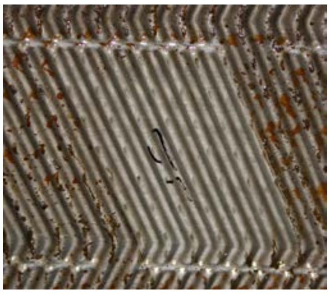

Fig. 7 – Area of a coated plate cleaned with a dry cloth showing that the easy to clean and repellent properties of the coating remained intact after 5 months in operation.

The permanent market test gives an indication regarding the repellent and easy to clean properties of a coating. In some areas of the coated plate no repellency was observed but the easy to clean properties were unaltered. In other areas/other plates the repellent properties were still evident (Fig. 7).

The plates were almost completely cleaned after high pressure water jet where only some minor deposits remained (Fig. 8).

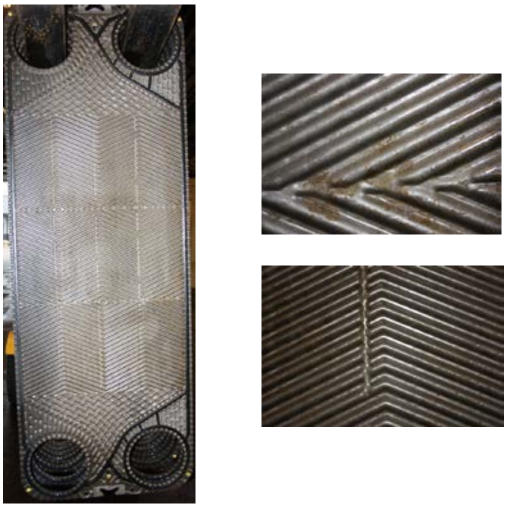

Fig.8 – Coated plate after high pressure water jet cleaning.

Coating degradation was observed in some plates mainly located at the edges adjacent to the long side of the plate (Fig. 9).

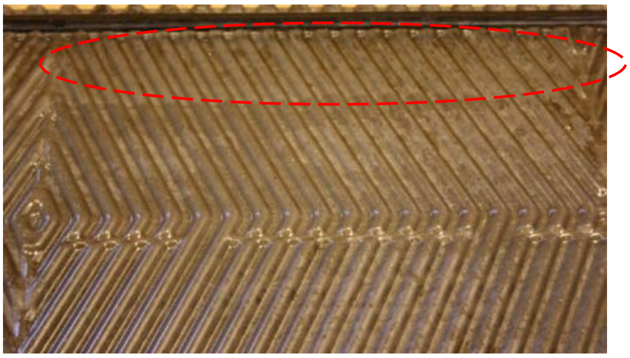

Fig. 9 – Coating degradation mainly located near the long sides of the plate. Degraded area is encircle in red (matt appearance).

The dry film thickness of the coating from different areas of the plate (heat transfer and distribution area – see fig. 6 where the locations of the cross sections are indicated by the yellow squares) varied from 4 to 11 µm (Fig. 10).

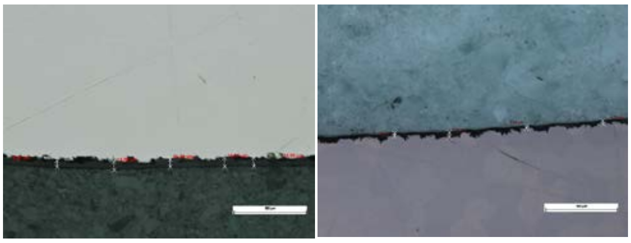

Fig. 10 - LOM photo of a cross section taken from the heat transfer (left) and distribution area (right) of a coated plate (see Fig. 6) where measurements of the dry film thickness gave values from 5 to 11 µm.

DISCUSSION

Adhesion of a substance to a substrate depends on surface properties such as roughness and surface free energy. It is observed, in general, that low surface free energies lead to minimal adhesion forces between the surfaces and deposit. An increase in the roughness of stainless steel surfaces was found to result in a larger wax deposition probably due to an increase of heterogeneous nucleation sites (Jorda, 1966). Therefore, a coating with both lower surface energy and lower roughness compared to the metal surface should reduce the amount of wax deposition. This was in fact observed in the present work where the ORC, having the surface energy and roughness reduced by half compared to the titanium surface (Table 2), decreased the amount of fouling (Fig. 5). In order to minimize adhesion and therefore fouling the surface energy of the metal surface should be lower than the surface tension of the foulant. The surface free energy of paraffin molecules in an orthorhombic lattice is low, where the end -CH_3 groups have a surface energy of about 30 mN/m and the side –CH_2- groups of about 36 mN/m (Wang and Ober, 1997). It is believed that the paraffin crystals are oriented with the end groups contacting the surface to minimize the total free energy of the system. From Table 2 it is seen that the ORC has a surface energy lower than the end groups of the paraffin molecules while the titanium surface has a higher surface energy.

The low adhesion forces between the coated surface and wax are also responsible for the different wax layer growth observed depending on the substrate. The weaker adhesive forces on the coated surfaces make it difficult for the wax molecules to attach in a coherent layer. However, once some wax molecules have already attached subsequent deposition will proceed on the deposited wax forming small islands on the surfaces. The same behavior was observed by Johnsen et al. (2011) when studying wax deposition on cold uncoated and coated steel.

The amount of fouling was found to depend slightly on the location of the plate in the plate pack where less fouling was observed in the first plates (near the frame plate). Kukulka and Leising (2010) while evaluating compact heat exchanger coatings determined different amounts of fouling depending on the position of the plates in the plate pack. For both large and small PHE a lower amount of deposit was also calculated in the beginning of the plate pack. This is related to the flow velocity which is somewhat higher on this location.

In general the coating presented a good stability after 150 days in the crude oil, however some coating degradation was observed in some of the plates. The location of these failures was mainly at the edges of the long sides of the plate (Fig. 9). The explanation could be related to the flow velocity and to the mechanical stresses which are larger at these locations. The thickness of the coating measured at different locations on one plate corresponded to the original thickness after coating application. This means that in the areas where the coating was present it was in a good condition.

Another aspect one needs to consider regarding coatings for heat exchangers is the influence the coating will have on the thermal performance of the PHE. The coating will act as a fouling layer in respect to the heat transfer, however due to the low thickness and reasonable thermal conductivity (~ 2 W / m K) of the present coating the reduction in heat transfer was estimated to be around 4%. It should also be noted that an uncoated heat exchanger with a thick wax deposit (low heat conductivity) will result in a lower thermal performance as compared to a coated heat exchanger where only a thin wax layer deposits.

The stability/repellency of the coating after the 2 years field test with the fully coated heat exchanger could not be evaluated so far but the lack of the need for reconditioning points to a good coating performance.

CONCLUSIONS

The conclusions of this study are as follows.

1. The coated plates in the partially coated plate pack showed a 65% decrease in the amount of fouling after 8 months operation.
2. Fouling adhesion to the coated plates was also reduced where the plates could be cleaned using only a high pressure water jet.
3. Only minor coating failures were observed on the fully coated unit after 5 months operation.
4. No stop for reconditioning was necessary with the fully coated plate pack during the 2 years field test, leading to an increase of operating time between maintenance of more than double.
5. The ORC proved to be successful in reducing fouling and improving cleanability in an offshore crude oil cooler heat exchanger.

NOMENCLATURE

PDMS	Polydimethylsiloxane
ORC	Oil repellent coating
SEM	Scanning electron microscopy
LOM	Light optical microscopy
PHE	Plate heat exchanger
WAT	Wax appearance temperature
sd	Standard deviation
γ^{TOT}	Total surface energy
γ^{LW}	Lifshitz-van der Waals component of the surface energy
γ^{+}	acid component of the surface energy
γ^{-}	base component of the surface energy

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