FOULING-RELEASE COATINGS FOR STEAM CONDENSERS IN THERMAL POWER PLANTS

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ABSTRACT

The application of anti-fouling coatings and fouling-release coatings on surface condensers of thermal power plants is discussed. Even though various commercial coatings developed for ship hulls exist, their direct application to condensers is not promising due to the coatings' thermal resistance. Biocide-free coatings were developed both based on silicone rubber and on sol-gel chemistry. In laboratory test simulating fouling adhesion, especially the silicone rubber based coatings provide low fouling adhesion even at a film thickness of merely 7 µm. For sea water exposure, a flow rate of 2 m/s was yet insufficient to keep the surfaces completely free of fouling. Industrial application requires both further development of the coatings and improved real-life testing.

INTRODUCTION

Biofouling, is an ubiquitous challenge for heat exchangers applying sea or fresh water as coolant. The accumulation of microorganisms, algae, plants or animals on the heat transfer surfaces affects both pressure drop and heat transfer. The present European project 'Matching' attempts to combat fouling in surface condensers by anti-fouling or fouling-release coatings as part of its general aim to reduce the cooling water consumption of thermal power plants, especially in areas with water scarcity. Herein, we discuss some considerations and preliminary results for the application of such coatings.

Today, power plants tolerate a certain loss in effectivity due to biofouling and/or combat biofouling, for example, by treatment of water with biocides, for example chlorine for sea water and Chloramin T (N-chloro 4-methylbenzenesulfonamide, sodium salt) for fresh water or by applying a sponge-ball cleaning system. While coating of surface condensers is not common, there is large experience as the hulls of marine vessels are coated with either an anti-fouling or a fouling release coating.

Anti-fouling coatings

Anti-fouling coatings dominated the marine market in the past. They are still the preferred choice for military and leisure boats that stay for long periods in the harbor as they are effective at low flow rates or even without flow. Anti-fouling coatings contain biocides. Following the ban on the environmentally adverse tributyl tin (TBT), common biocides are, for example, copper (I) oxide, copperpyrithine, zinc ethylene-1,2-bis-dithiocarbamate (zineb) or 2-methylthio-4-tert.-butylamino-6-cyclo-propylamino-s-triazineare. To be effective, the biocides leach out of the coating. To continuously provide biocide, practically all anti-fouling coatings are self-polishing. The coating material continuously erodes to provide a new surface that is still loaded with biocide. Lifetimes up to 7.5 years can be reached (Jotun, 2017). However, this requires that the top coat alone has a film thickness of 75-175 µm, which has significant impact on heat transfer. Furthermore, the typically elevated temperatures, at which heat exchangers operate, increase leaching and decrease lifetime. The application on heat exchangers is thus not straightforward.

Fouling release coatings

Fouling release coatings are today widely applied on merchant ships and ferries. They do not necessarily prevent the growth of fouling and often tolerate a thin slime layer (Yebra, 2004), but provide low fouling adhesion and allow the flow to detach larger macrofouling. They are non-sacrificial, and typically free of biocides, although combinations of fouling release and anti-fouling exist (Hempel, 2017). Most fouling release coatings are based on silicone rubber (Morris et al., 2008, Thorlaksen and Blom, 2011), partly in combination with additives that provide a hydrophilic surface (Webster and Bodkhe, 2015, Olsen et al., 2016). Depending on the type of fouling, these coatings require a specific drag that is typically reached at cruise speeds of 7 knots (ca. 3.6 m/s), or even higher (Yebra et al., 2004). This is higher than the typical flow rate of steam condensers in power plants of 2 m/s. An advanced commercial fouling release coating based on a perfluoroalkyl-silicone hybrid polymer, providing low adhesion and surface hydrophilicity, claims to reduce fouling to some extent already at a speed of 2 knots (~1 m/s). (AkzoNobel, 2017). These coatings are typically applied at a thickness of 140 to 200 µm.

While fouling consists of various organisms, a severe challenge is caused by the strong adhesion of barnacles. Barnacles can cut through existing biofilm and in some cases even through coating layers (Transocean, 2017, Townsin and Anderson, 2009). This has led to specific testing for barnacle adhesion (ASTM, 2011) to evaluate a coating's fouling release performance. Swain et al. (1997) discovered for silicone coatings that removal of epoxy studs glued to the dry surfaces results in adhesion forces similar to those of real living barnacles on wet surfaces. Since then, various surfaces have been tested with various adhesion tests based on epoxy adhesives, both in shear mode and in pull-off mode, under the umbrella term 'pseudo barnacle test' (Kohl and Singer, 1999; Stein et al., 2003; Xie et al., 2012; Popa et al., 2015).

An adhesion theory for hard objects (herein, barnacles and epoxy are considered as 'hard') glued to elastomeric coatings, that themselves have been applied to a stiff substrate (f. ex. steel), has been formulated by Kendall (1971) and extended by Kohl and Singer (1991). A result of Kendall's theory is outlined by Eq. (1), showing that the pull-off force $F_{pull\text{-}off}$ is lowest, when the bulk modulus K of the coating is low (the coating is 'soft'), the work of adhesion w_a is low and the coating film thickness d is high. The referenced literature provides additional advanced equations for multi-layer coating films.

$$F_{pull\text{-}off} \propto w_a^{1/2}\, K^{1/2}\, d^{-1/2} \qquad (1)$$

Fouling release coatings are interesting for heat exchangers, as they are more environmentally friendly than anti-fouling coatings due to the absence of biocides. Challenges are the flow rates in condensers that are typically lower than the cruising speed of marine vessels. Furthermore, the coatings would need to be effective at low thickness, as otherwise the thermal conductivity is compromised

Thermal conductivity of coating films

When applying a coating to heat exchangers, the beneficial effect needs to outperform the thermal resistance of the coating film itself. The requirement for the coating's heat conductivity is individual for each application, depending on possible fouling reduction and on the overall heat transfer coefficient U_0 of the respective uncoated heat exchanger. The following consideration does not take the fouling reduction into account, but highlights why thin coatings, typically in the range of a few µm, are required. The thermal conductivity k of an epoxy polymer, which is frequently applied for commercial, organic coatings is, according to Czichos (2000), around 0.2 W m^{-1} K^{-1}. Data for various other polymers (Czichos, 2000; EgineeringToolBox, 2017) suggests that most organic coatings and organic-inorganic hybrid coatings are within this order of magnitude. Thus, the main parameter to influence heat transfer coefficient h_{coat} of a coating film is the coating thickness d, as illustrated by Fig. 1 according to Eq. (2).

$$h_{coat} = k/d \qquad (2)$$

The overall heat transfer coefficient U_{coat} of a coated heat exchanger can be calculated from U_0 and h_{coat} according to Eq. (3).

$$U_{coat} = 1/(U_0^{-1} + h_{coat}^{-1}) \qquad (3)$$

Equation (4) provides the relative reduction ΔU_{rel} of the overall heat transfer coefficient U_0 by a coating film. According to EngineeringToolBox (2017a), U_0 of a surface condenser is typically between 1500 and 4000 W m^{-2} K^{-1}. Choosing typical values of U_0 = 2500 W m^{-2} K^{-1} and thermal conductivity k = 0.2 W m^{-1} K^{-1} for the coating, Fig. 2 provides the reduction of U_0 by the coating film according to Eq. (4), and outlines that a coating film significantly decreases the heat transfer of common surface condensers when the coating film thickness is larger than a few µm.

$$\Delta U_{rel} = (U_0 - U_{coat})/U_0 \qquad (4)$$

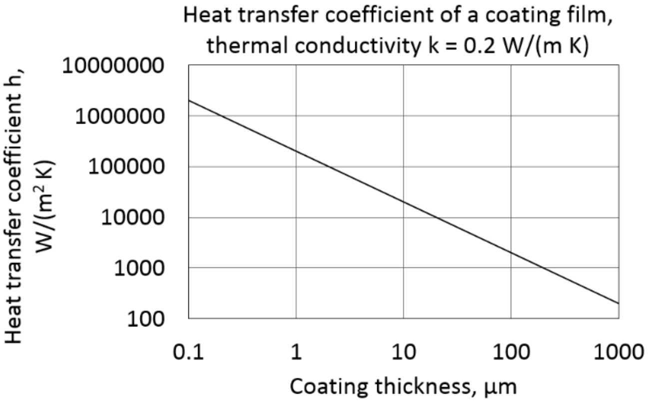

Fig. 1 Effect of coating thickness d on the heat transfer coefficient h_{coat}.

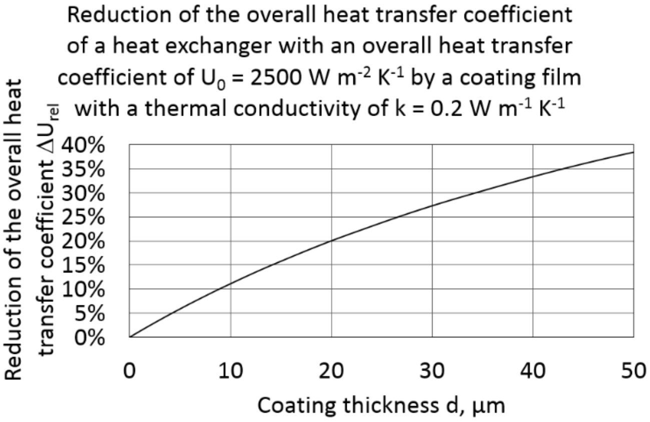

Fig. 2 Effect of coating thickness on the overall heat transfer coefficient.

EXPERIMENTAL

Surfaces

'316 steel' and 'SAF 2205 steel' are stainless steels, SAE grade 316 and duplex SAF 2205, respectively. For the pseudo barnacle test, coatings were applied direct to '316 steel', for the sea water exposure test, 'SAF 2205 steel' was first coated with an epoxy primer and a polyurethane coat, and then with the respective top coat.

'SiRu1', 'SiRu2', 'SiRu3' and 'SiRu3-PEG' are moisture curing silicone rubbers, all applied by wire wound rods (flat '316 steel' samples), dip-coating (pins) or paint brush ('SAF 2205 steel' samples) and cured 20h at ~20°C. 'SiRu1' and 'SiRu2' are prepared from 79 parts silanol-terminated polydimethylsiloxane (PDMS) with a molecular mass of 18 000 g/mol for 'SiRu1' and 110 000 g/mol for 'SiRu2', respectively, 20 parts of a silane cross-linker and 1 part dibutyltin dilaurate (DBTL) catalyst. 'SiRu3' is prepared from 97.5 parts 3-({[3-(trimethoxysilyl)propyl]carbamoyl} amino)propyl-terminated PDMS with a molecular weight of 30000 g/mol and 2.5 parts of a transition metal curing catalyst. 'SiRu3-PEG' is prepared from 97.5 parts of different 3-({[3-(trimethoxysilyl)propyl]carbamoyl}amino)propyl-terminated polymers and about 2.5 parts of a transition metal curing catalyst. The polymers for 'SiRu3-PEG' being mainly PDMS with a molecular weight of 30000 g/mol, but also PDMS with a higher molecular weight due to dimerization, and about of 6 parts a block-copolymer formed by two terminal PDMS units with a molecular weight of 30000 g/mol and one poly(ethylene glycol) (PEG) unit in the middle with a molecular weight of about 6000 g/mol to render the coating more hydrophilic

'Silic One' is a commercial, marine fouling release coat by Hempel, based on silicone rubber and additives that render the surface more hydrophilic. It is applied on top of Silic One Tie coat by paint brush for the 100 µm film and by spraying after dilution with triethoxymethylsilane for the 9 µm film. Each layer was cured 20 h at ~20°C. The overall film thickness of both layers is provided.

'SolGel1' and 'SolGel2' are organic-inorganic hybrid coatings prepared by sol-gel processing. They have been previously published by Bischoff and Holberg (2015) as examples 1 and 2, respectively. They were applied by spraying and cured 1h at 200°C.

'Epox1' and 'Epox2' are commercial, pigmented, two-component epoxy top coats. 'Epox1 (EP 200-90 by Mipa) was, applied by spraying and cured 3 h at 60°C. 'Epox2' (Chemglide by Chemco) was applied by paintbrush and cured one day at ~20°C.

Analysis

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

Pseudo-barnacle test: The test was performed by gluing aluminum studs with a diameter of 20 mm onto coated plates (316 steel, 1.5 mm thick) using an epoxy adhesives (UHU Plus sofortfest, cured 10 min at 90°C) and pulling the studs off with a Positest AT-A by DeFelsko at a rate of 0.2 MPa/s (cf. Fig. 3). An average of six measurements for each surface is provided.

Pin pull: A cylindrical aluminum pin, d=10 mm, coated with the respective coating, was on its side on 40 mm length mold into a two-component polyurethane resin and pulled along its axis out of the polyurethane, measuring the maximum force and calculating the pressure to release the pin (cf. Fig. 3). The test was repeated seven times for each pin. The average of three pins with the same coating is provided.

Strip pull off. A cotton strip, width 30 mm, was impregnated with a two-component polyurethane resin and glued to stainless steel plates coated with the respective coatings. The strip was removed by pulling it off perpendicular to the surface, measuring the maximum force and calculating the maximum tension to release it (cf. Fig. 3). The test was repeated 11 times on the same spot for each sample. The average of three samples for each surface is provided.

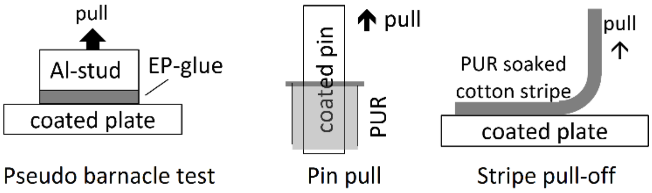

Fig. 3 Schematic of different adhesion tests.

Exposure to sea water. Coated plates were immersed for 64 days in sea water at 15-27°C in a raceway reactor with a flow of 2 m/s in an algae plant in Litoral in southern Spain. The sea water comprises ca. 0.9 g/l of the microalgae *Nannochloropsis gaditana*, which thus accelerates the growth of this algae on the plates. The plates were mounted with their surfaces parallel to the flow. After exposure, the plates were dried, and weighed on a WLC2/A2 analytical balance. The plates were then cleaned from fouling and weighed again to determine the weight difference that represents the amount of fouling.

RESULTS AND DISCUSSION

Pseudo barnacle test

The suitability of different coatings for fouling release was evaluated by a pseudo-barnacle test; Table 1 provides the results. The adhesion of the epoxy glue applied as pseudo-barnacle is a magnitude lower on all tested silicone rubber or sol-gel coatings as compared to bare stainless steel or a standard epoxy coating. Thus, these surfaces are promising for fouling-release applications, even at low film thickness of 4 to 7 µm.

The results do not fully comply with the theory of Kendall (Eq. 1) with respect to bulk modulus, work of adhesion and coating thickness. The bulk modulus was not precisely determined, but manual handling of the coatings reveals, that the bulk modulus of SolGel1 and Solgel2 is at least one magnitude higher than the bulk modulus of SiRu1 and SiRu2, and the bulk modulus of the epoxy coating is between that of the Sol-Gel coatings and the silicone rubbers. When comparing SiRu1 and SolGel1, both coatings provide a similar surface tension and show comparable pseudo barnacle adhesion, even though SolGel1 is thinner and has a significantly higher bulk modulus, which both should lead to higher adhesion according to Kendall's theory. When comparing SiRu1 at different thicknesses, the lower thickness did not lead to higher adhesion (as would have been expected). However, Kendall's theory requires a certain coating thickness to allow sufficient deformation. We speculate that the thickness of the coatings of maximal 22 µm is already too low, so deformation that could facilitate pseudo-barnacle detachment is negligible, independent of bulk modulus and exact thickness. At present, the higher pseudo-barnacle adhesion of SiRu2 compared to SiRu1 could not be explained.

Table 1 Pseudo-barnacle adhesion and fouling obtained in the algae plant.

Surface (film thickness in µm)	Pseudo barnacle adhesion in MPa	Fouling in algae plant in g
316 steel	>10 (broke between stud and glue)	not tested
SAF 2205 steel	not tested	0.00 / 0.01 / 0.03
Epoxy1 (18± 3)	3.9 ± 0.9	not tested
Epoxy2 (~100)	not tested	0.43
SiRu1 (~50)	not tested	0.57
SiRu1 (22± 3)	0.33 ± 0.06	not tested
SiRu1 (7 ± 3)	0.33 ± 0.04	not tested
SiRu2 (13 ± 3)	0.66 ± 0.10	not tested
SiRu3 (~50)	not tested	0.84
SiRu3-PEG (~50)	not tested	0.23
Silic One (~100)	not tested	0.04 / 0.14
Silic One (~9)	not tested	0.11 / 0.11
SolGel1 (4 ± 1)	0.22 ± 0.09	0.05
SolGel2 (4 ± 1)	0.50 ± 0.11	0.04

The work of adhesion can be calculated from contact angle measurements and surface tensions, the theory is described by van Oss et al. (1988), Rosmaninho et al. (2004), and Smith et al. (2012). Surface tensions of SiRu1 (γ_{tot} = 18.6 mN/m), SolGel1 (γ_{tot} = 21.1 mN/m), SolGel2 (γ_{tot} = 31.2 mN/m, all Holberg and Bischoff, 2014) and 316 steel (γ_{tot} = 53 mN/m, Rosmaninho, 2004) have been previously determined. The differences in surface tension may explain the different pseudo barnacle adhesion of SolGel1 and SolGel2, but are expected to be insufficient to explain the huge adhesion differences between 316 steel and epoxy on one side and all sol-gel and silicone rubber systems on the other side. It should be mentioned that the work of adhesion is fundamentally different in water as compared to the pseudo barnacle test that is carried out in air.

Possible further explanations for the pseudo-barnacle results may be the low surface roughness of all sol-gel and silicone rubber surfaces, or a new concept of interfacial slippage introduced by Beemer et al. (2016) and Golovin et al. (2016), developed from work on anti-ice coatings. They introduce interfacial slippage as a further parameter relevant for adhesion. Independent from the bulk modulus, mobile polymer chains at the surface reduce adhesion. Polydimethylsiloxane chains, the main component of silicone rubber and an additive in SolGel1, are especially mobile.

Durability

In addition to the pseudo barnacle test, the adhesion of a polyurethane resin to SiRu1 and SolGel1 was repeatedly tested (table 2). While this is not a designated fouling-release test, the results are still relevant for further development, as they outline advantages of silicone rubber over the sol-gel coating. The pin-pull test, a shear test, initially provides similar results for SiRu1 and SolGel1, while the pull-off test of a cotton strip shows that, in this test mode, the softer silicone rubber provides significantly lower adhesion. The repeated test on the same spot with 7 or 11 repetitions, respectively, clearly shows that the low-adhesion properties of SolGel1 degrade more quickly than those of SiRu1. There is no visible degradation of SolGel1. However, according to Holberg and Bischoff (2014), the silicone additive of SolGel1 forms an ultrathin layer at the coating surface, that may be degraded by repeated testing. In contrast, silicone rubber like SiRu1 provides silicone as bulk material.

Table 2: Pin pull (shear) and strip pull-off adhesion of a polyurethane casting resin.

Surface	Max. pressure 1st pin pull in MPa	Max. pressure 7th pin pull in MPa
SiRu1	1.5 ± 0.0	2.3 ± 0.1
SolGel1	0.95 ± 0.14	4.4 ± 0.1
Surface	Max. tension 1st strip pull-off in N/m	Max. tension 11th strip pull-off in N/m
SiRu1	16 ± 10	37 ± 17
SolGel1	90 ± 27	1000 ± 300

Sea water exposure in an algae plant

Table 1 provides the mass of algae fouling after 64 days sea water exposure. If more than one specimen per surface was tested, results for each specimen are provided. The force needed to remove the fouling was not recorded. Figure 4 shows exemplary heavy (SiRu3) and light fouling (SolGel2).

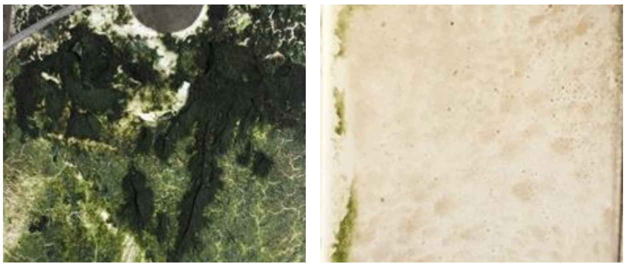

Figure 4 Algae fouling on SiRu3 (left) and SolGel2 (right), showing 45 x 50 mm sections.

The lowest amount of fouling was provided by the uncoated steel coupons. As steel in general does not provide good release properties, we expect the result to be due to low fouling growth on steel as compared to all coatings. This could during 64 days testing at a flow rate of 2 m/s not be outperformed by any potential fouling release properties of the coatings. Regarding the differences between the coatings, it is not obvious whether these are caused by a different fouling growth rate, or by fouling release properties of some of the coatings. Thus, it is not obvious, why both sol-gel coatings, the commercial Silic One coating and to some extent also SiRu3-PEG performed better than the bare silicone rubbers SiRu1 and SiRu2 and better than the organic Epoxy2 coating. While both Silic One and SiRu3-PEG comprise a hydrophilic additive, the performance of the sol-gel coatings was not influenced by the higher hydrophobicity of Sol-Gel1 due to the PDMS additive as compared to Sol-Gel2.

CONCLUSIONS

1. Commercial anti-fouling and fouling-release coatings for ships cannot directly be applied to steam condensers as the coating thickness, and thus the thermal resistance is too high.
2. In the limited scope of the present sea-water-exposure test, bare stainless steel outperformed all coatings.
3. However, attempts to further improve fouling release coatings with a thickness below 10 µm based on silicone rubber, potentially in combination with hydrophilic additives and thus similar to commercial coatings, are promising due to low pseudo-barnacle adhesion, due to an indication that the hydrophilic additive may reduce algae growth, and due to the significantly better durability of silicone rubber in the repeated release tests as compared to the otherwise also well-performing sol-gel coatings.
4. More research, as already planned as part of the EU-project 'Matching', is necessary, both to understand the adhesion behavior, but also to obtain improved real-life results from heat exchangers.

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NOMENCLATURE

d	coating film thickness, m
h_{coat}	heat transfer coefficient of a coating film, $W/(m^2\ k)$
$F_{pull\text{-}off}$	pull-off force, N
K	bulk modulus of a solid, $K = V\ dp/dV$ with V as volume and p as pressure, Pa
k	thermal conductivity, W/(m K)
w_a	work of adhesion per surface area, work to separate to adjacent phases, J/m^2
U_0	overall heat transfer coefficient (e.g. of a heat exchanger), without coating, $W/(m^2\ K)$
U_{coat}	overall heat transfer coefficient (e.g. of a heat exchanger), without coating, $W/(m^2\ K)$
ΔU_{rel}	Reduction of the overall heat transfer coefficient (e.g. of a heat exchanger) caused by a coating film, dimensionless
γ_{tot}	Total surface tension of a solid, N/m

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