**Supplementary material**

**Innovative fouling-resistant materials for industrial heat exchangers: a review**

Caroline Françolle de Almeida et al.

DOI 10.1515/revce-2020-0094

**Tables corresponding to section 3.3.1 Antifouling/fouling release strategies**

**Supplementary Table S1:** Dairy fouling.

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Substrate** | **Treatment** | **Result** | **WCA (°)** | **SFE (mN/m)** | **Ra/Sa (µm)** | **Thermal conductivity (W/m.K)** | **Thickness (µm)** | **Classification** | **Properties** | **Durability/Stability/Reusability** | **Fouling/clean ability test conditions** | **Ref.** |
| SS | Epoxy + NP/polyurethane + NP/PTFE |  | 91/93/  86 | - | Ra  0.95/0.06/  1.35 | - | 85.2/83.7/  22.5 | Hydrophobic | AF/FR | Under pasteurisation conditions: coating destroyed at the contact point | Pasteurisation (PHE): WPC, inlet Tbulk 85 °C, flow rate 1.5 L/h, for 4 h | (Kananeh et al., 2010) |
| SS | PTFE-CNT |  | 141 | 0.89 | - | 10.25 | 11 | Hydrophobic | AF | - | Pasteurisation with liquid recirculation (custom-designed PHE): pasteurised milk, inlet Tbulk 60 °C, flow rate 53 mL/min, Re number 171, for 1, 3, 5 h | (Rungraeng et al., 2012) |
| 316 SS | Ni-P-PTFE |  | - | 24.7 | Ra  0.17 | - | 10.45 | - | AF | No significant difference in the amount of fouling material after 10 sequential 4-h pasteurisation cycles followed by a low-flow rinse | Pilot plate heat exchanger  Model fluid: pasteurised milk, from 65-85 °C, flow rate 36L/h, Re number 256,  For 8 h | (Barish and Goddard, 2013) |
| SS | DLC/SICAN/SICON® | **-** | - | 45/46/46 | Ra  0.13/0.12/  0.12 | 0.3-1.3 | 3 | - | AF | - | Batch pasteurisation, SMUF, WPI, SMUF + WPI, inlet Tbulk 50 °C and 40 °C for SMUF only,  Tsubstrate 80 °C, 120 °C, 105 °C,  60 rpm, Re number 12, for 6 h | (Boxler et al., 2013) |
| 316 2B SS | Doped DLC | **-** | 57/61/  51 | 48/44/41 | Ra  0.2/0.15/  0.13 | - | - | Hydrophilic | AF/FR | - | Pasteurisation (PHE): Skim and whole milk, WPI solutions, from 68 to 84 °C, volumetric flow rate 99.7 L/h , Re number 1100 (in the final PHE) for 2, 4, and 8 | (Patel et al., 2013) |
| 316L SS | Thermolon (inorganic ceramic polymer) |  | 105.5 | 32.4 | Sa  199.0 | - | - | Hydrophobic | AF/biofilm formation | - | Pasteurisation (benchtop scale): raw whole milk, Tbulk from 40 to 85 °C, flow rate 1.32 L/h, for 7.5 h | (Liu et al., 2017) |
| 304 2R S | PFA/FEP/PTFE | **-** | 108/108/81 | 16.9/16.9/223.8 | (Sa) 0.56/0.38/  0.74 | 0.27/0.15/0.12 | 71.2/57.8/41.8 | Hydrophobic/Hydrophilic | AF | - | Pasteurisation with liquid recirculation (bench scale): WPC and raw milk, , inlet T 61 °C, Tsubstrate 89 °C with WPC and 92.5 °C with raw milk flow rate 480 L/h, Re number 6900 for milk and 11100 for WPC, for 2.5 h | (Magens et al., 2019) |
| 316L 2B SS | PEO – modified silicone |  | Instant WCA 105 ° | 0.02 | - | - | - | Amphiphilic | AF/FR | After 5 pasteurisation cycles WCA = 46 °, Before and After CIP: WCA from 112 ° to 98 ° | Pasteurisation (PHE) : Model fluid: WPI and calcium solution, Tbulk from 60-85 °C, flow rate 300 L/h, for 1.5 h | (Zouaghi et al., 2018) |
| SS | Fluorolink® S10 (PFPE with triethoxysilane terminal groups) | **-** | 107 | 19.0, after rinsing 32.0 | - | - | < 2.7 | Hybrid | AF/FR | - | Pasteurisation with liquid recirculation (bench scale): WPC, inlet Tbulk 61 °C, Tsurface > 100 °C, flow rate 4.7 × 10-3 kg/s, for ≈1 h | (Huo et al., 2019) |

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**Supplementary Table S2:** Petrochemical fouling:

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Substrate** | **Treatment** | **Result** | **WCA (°)** | **SFE (mN/m)** | **Ra (µm)** | **Thermal conductivity (W/m.K)** | **Thickness (µm)** | **Classification** | **Properties** | **Durability/Stability/Reusability** | **Fouling/clean ability test conditions** | **Ref.** |
| CS | Polyurethane/Epoxy resin/ferrous phosphate/PTFE/PFA | - | 119/131/45/91/92 | - | - | - | 1000 | Lipophilic/lipophilic/hydrophilic/hydrophobic/hydrophobic | AF | - | Bench scale: crude oil and n-heptane, Tbulk 20-25 °C, to 40 h | (Moradi et al., 2019) |
| SS | NANOmel (silicon oxide) | - | 45/85 | - | 0.35/0.42 (Ridge) | - | 0.4 | Hydrophilic/hydrophobic | AF | Uncoated unit was blocked after 3 days while the coated units were only stopped after a period of 6 days | PHE run with hard tap water, 2 L/min, Tbulk 88 °C, for 7 days | (Christiensen et al., 2017) |
| Titanium | Urea-siloxane modified with 2 % of PDMS | - | 105 | 21 | - | - | 2-5 | Hybrid | AF | Attack by acetone wiping | PHE: crude oil cooling, Tbulk from 50 to 40 °C, to 8 months | (Holberg and Bischoff, 2014) |
| SS | PFPE | - | 138 | 46 | - | - | 5000 | Hybrid | Anti-scaling/FR | Immersion in a NaCl solution at 50 °C, for 7 days: WCA 129 ° before immersion, and WCA = 62 ° after immersion | Pilot plant (two shell-and-tube heat exchangers) Model fluid: water at 60 °C, flow rate 184 L/h (laminar flow) For 5 months | (Oldani et al., 2016) |

**Supplementary Table S3:** Energy fouling.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Substrate** | **Treatment** | **Result** | **WCA (°)** | **SFE (mN/m)** | **Ra**  **(µm)** | **Thermal conductivity (W.m/K)** | **Thickness (µm)** | **Classification** | **Properties** | **Durability/Stability/Reusability** | **Fouling/clean ability test conditions** | **Ref.** |
| Steel | Ni-Cu-P-PTFE |  | 105 | 0.02 | 0.6 | - | - | Hydrophobic | Anti-scaling | Immersion in boiling water for 20 h | Flow pool boiling test rig: Immersion in boiling water for 4 h during 20 h | (Cheng et al., 2014) |
| 316L SS | Polymer brushes: N-POEGMA9 / N-POEGMEMA9 | - | 34.8/ 42.5 | - | - | - | 0.02/0.014 | Hydrophilic | Anti-scaling | - | PHE: water solution, Tbulk from 20 to 80 °C, flow rate 120 L/h, Re number 605, for ≈ 165 h | (Friis et al., 2019) |
| 316L steel | Silicone-PEG-PDMS | - | 109 | - | - | - | ~ 10 | Hydrophobic | Biofouling release | No visual degradation after run | Tubular heat exchanger: Freshwater solution at 40 °C, flow 1.6 m/s for 2 months | (Holberg et al., 2020) |
| 316L SS | DLC/F-DLC | - | 70/ 81.3 | 46/28 | 0.017/0.020 | - | 1 | Hydrophile | Anti-biofouling/FR | - | Adhesion with *Pseudomonas fluorescens* | (Su et al., 2010) |

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**Tables corresponding to section 3.3.2 Antifouling/fouling-release materials with extreme wettability and/or biomimetic**

**Supplementary Table S4:** Dairy fouling.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Substrate** | **Texturing technique** | **Chemical treatment** | **Results** | **WCA/SA (°)** | **Ra (nm)** | **Thickness (µm)** | **Classification** | **Properties** | **Durability/Stability/Reusability** | **Fouling/clean ability test conditions** | **Ref.** |
| 420 martensitic SS | Picosecond laser | Immersion in stearic acid |  | 163/0.5 | - | - | Superhydrophobic | Antibacterial adhesion | Immersed in the NaCl (0.5 mol/L) = 30 days | - | (Pan et al., 2019) |
| 316 SS | Electrodeposition | PEDOT-F4 |  | WCA  162/2 | 244 | - | Superhydrophobic | Bacterial adhesion | - | - | (Bruzaud et al., 2017) |
| Plaster | Hydrothermal process | Colourful mineral pigments | - | 150/- | - | - | Superhydrophobic | AF | Heating at 70 °C and 85 % HR | Milk, coffee, Coca Cola droplets deposition on the painted surfaces | (Wang et al., 2020) |
| SS | Vacuum evaporation, chemical reaction and heating | Cu film + Ag NPs + Fluor compound |  | 155/ 0 | - | 0.22 | Superhydrophobic | AF/Self-cleanability | Immersion into solutions pH (1, and 13) : WCA ≈ 151 ° Exposition in air for 30 days : WCA = 156.3 ° | Immersion into milk in static conditions for 24, 48 and 72 h | (Wang et al., 2019) |
| SS 316 L 2B | Femtosecond laser ablation | Fluorosilane and perfluorinated compounds |  | 111.6/- | - | - | SLIPS | AF | 1 pasteurisation cycle (90 min) | Plate heat exchanger (WPI and calcium solution T= 85 °C)  Flow rate 300 L/h | (Zouaghi et al., 2017) |
| Glass, Al and Si | Immersion into precursor solution, spin coated, UV | TEOS, VTES, POTS, SiO2, PFPE | - | 112/- | RMS 18.3 | - | LIS | AF/self-cleaning | Knife scratching measured/ WCA and SA measured at 60 °C for one week (WCA = 115 ° and SA = 4 °) | Vertically dipped into milk 60 times (glass substrate) | (Li and Guo, 2019) |
| Zn | Grafting reaction | ZnO + PDMS + silicone oil | - | 140/3 | - | - | LIS | AF | Immersion boiling water/Heated at 120 °C for 15 min/Shearing stress for 60 s, long-term immersion for 400 h and strong acid/alkali | Soaked in milk | (Jing and Guo, 2019) |

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**Supplementary Table S5:** Petrochemical fouling.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Substrate** | **Texturing technique** | **Chemical treatment** | **Results** | **CA/SA (°)** | **Ra (nm)** | **Thickness (µm)** | **Classification** | **Properties** | **Durability/Stability/Reusability** | **Fouling/clean ability test conditions** | **Ref.** |
| Silicon wafer | - | Polymers brushes (PMPC) | - | WCA < 3, under water OCA = 173 ° | 0.8-1.5 | 0.04 | Superhydrophilic | Antifouling/Self-cleaning | - | Oil detachment behaviour in water | (Kobayashi et al., 2012) |
| CS | Zn electrodeposition | Phosphatation and deposition of a silica film |  | under water OCA 164.5 ° | - | - | Superhydrophilic | Antifouling/high T resistance | Heating until 200 °C of 48 h  WCA = 0 ° | Wax deposition by cold-finger method (crude oil at 80 °C) | (Liang et al., 2015) |
| 304 SS | Oxidation | - |  | WCA > 5 °  Under water OCA 164 ° | - | - | Superhydrophilic | Antifouling/Self-cleaning | Heating until 500 °C for 1 h (OCA 160 °) | Crude-oil detachment washed by water | (Peng et al., 2018) |
| Steel | Electrostatic powder spraying | PSU - CNTs-FEP |  | WCA  166.0 ° / SA < 5 ° | - | - | Superhydrophobic | Self-cleaning and corrosion inhibition | Heating until 500 °C  WCA ≈158 °  0CA ≈148 ° | Sliding water droplet on the contaminate substrata | (Zhu et al., 2018) |
| 304 SS | Electrodeposition/thermal reaction | Ni3S2 |  | WCA = 163 ° | 149 | 0.0103 | Superhydrophobic | Antifouling | Plasma and heating (300 °C) cycles | Immersion into kerosene and rinsed by deionized water | (Yin et al., 2020) |
| Cu | Anodization | CuO nanowire + FAS 17 |  | WCA 154 ° | - | 0.5 | Superhydrophobic | Anti-scaling |  | Immersion in a mixed solution of CaCl2 and NaHCO3 at 90 °C for 2 h | (Jiang et al., 2015) |
| Steel | Electrodeposition | Immersion into alkaline solution + fluorination |  | WCA 157 ° | - | - | Superhydrophobic | Anti-scaling | Thermal stability at 200 °C for 1 h/Abrasion test | Immersion in a mixed solution of CaCl2 and NaHCO3 at 70 °C for 6 h | (Li et al., 2016) |
| Steel | Electrodeposition | Cu-Zn |  | WCA 154.7 ° / SA 6.5 ° | - | - | Superhydrophobic | Fouling release | Heating (temperature varying from 20 °C to 200 °C for 9 h | Immersion in a CaCO3 solution | (Li et al., 2019) |
| Ni | Electrodeposition/thermal reaction | Ni3S2 + Myristic acid |  | WCA 165 ° / SA 3 ° | - | - | Superhydrophobic | Anti-scaling | Plasma and heating (300 °C) cycles | Immersion into supersaturated CaCO3 solution at 60 °C for 6 h | (Yin et al., 2019) |
| Q235 CS/304 SS | Spray/cure | PPS + PTFE | - | 45 % PTFE (WCA 160 °) | - | - | Superhydrophobic | Anti-scaling | - | Immersion into CaCO3 solution at 60 °C for up to 360 h | (Qian et al., 2017) |
| 316 SS | Chemical etching and O2 plasma | OTS and silicone oil | - | WCA  120.4 ° | 314 | - | LIS | High-T resistance and anti-wetting | Heating until 600 °C of 30min  WCA = 87.8 ° | - | (Zhang et al., 2016) |
| SS 316 L | Electrodeposition | PPy -  BMIm |  | WCA  71.0 ° | - | 5 | SLIPS | Anti-scaling | After immersion in seawater for 24 h, advanced and receding CA remained unchanged | Immersion into brine solution at 50 °C, static conditions, for 2 h (Standard bulk jar test) | (Charpentier et al., 2015) |
| 1020 CS | Electrochemical | HDFDPA  Krytox ® |  | WCA  120.0 ° | - | - | SLIPS | Anti-scaling/ and corrosion inhibition | 40 h in fouling test conditions | Immersion without turbulence into brine solution at room T | (Sousa et al., 2020) |

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**Supplementary Table S6:** Energy fouling.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Substrate** | **Texturing technique** | **Chemical treatment** | **Results** | **WCA (°)** | **Ra (nm)** | **Thickness (µm)** | **Classification** | **Properties** | **Durability/Stability/Reusability** | **Fouling/clean ability test conditions** | **Ref.** |
| PVC | Photopolymerisation | PHEMA | - | 0 | - | - | Superhydrophilic | Anti-scaling | Heating until 80 °C for 24 h | Incubation in a flowing CaCO3 solution at 80 °C, for 24 h.  Adhesion of mineral crystals at room T in dynamic and static conditions | (Zhang et al., 2018) |
| 304 SS | Spray coating | PMMA and BN | - | Modified 142), PMMA (133 °) and BN (135 °) | - | - | Superhydrophobic | Anti-scaling | Increase pressure drop on modified and PMMA PHE | PHE: in tap water solution, Tbulk from 25 to 60 °C solution, flow rate 0.133 kg/s, for 2 h | (Ahn et al., 2019) |
| Steel | Atmospheric plasma | Fluorosiloxane and fluoropolymer | - | TCFS (152 °) TC (158 °) | 10/17 | 0.130/0.290 | Superhydrophobic | Anti-scaling | Wear resistance test: delamination occurred at the contact points | Laboratory scale heat exchanger: recirculation CaCO3 solution, Tbulk from 32 to 32.4 °C solution, fluid velocity 0.30 m/s, for ≈ 17 h | (Dowling et al., 2010) |
| Ti | Electrochemical deposition and CVD | Dimethyl silicone oil |  | - | - | 20 | SLIPS | Anti-biofouling | - | Immersion into algae suspension in seawater (static conditions) for 7 and 14 days | (Ouyang et al., 2019a) |
| SS | Electrodeposition | Polydopamine + Benzophenone + Diphenylamine |  | 82 ° | - | 40 | SLIPS | Inhibition of MIC | - | Immersion into algae suspension in seawater (static conditions) for 1, 7 and 14 days | (Ouyang et al., 2019c) |
| Cu | Electrodeposition of cobalt dendrite | Polydopamine, dodecanethiol, dimethyl silicone oil |  | 96 ° | - | - | LIS | Inhibition of bio-adhesion/MIC | - | SBR attachment: Immersion in a culture medium incubated with SBR at 30 °C, at 24 h | (Ouyang et al., 2019b) |
| Al | Anodization | PFDS/PFPE |  | - | - | - | SLIPS | Inhibition of SBR adhesion | Null toxicity of the lubricant | Immersed into a 3-days-old culture solution | (Wang et al., 2015) |

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