Crowne Plaza Hotel
Baton Rouge, LA

Global Solutions SYMPOSIUM 2024

High-Temperature Stable, Hydrophobic Coatings for Antifouling Applications

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Track: Emerging Technology

Sustainable Process Industries

Hydrophobic Coatings in Process Equipment

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Hydrophobic Coatings in Process Equipment

Outline and Rationale

1. Emissions Reduction
   - Global need to lower emissions - reduced fouling rates may reduce CO_2
2. Benefits of Hydrophobic Coatings
   - Lowers surface energy, % surface polarity (SP). May protect against corrosion, oxidation & carburization
3. Laboratory Experiments
   - Fouling rate reduction, measurements of surface energy & polarity
4. Industrial Field Trials
   - Vacuum wash beds, Heat exchangers

Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Minimox® Alloy Treatment

- Not a traditional coating, more like surface doping.
- Water-based product yields scattering of rare earth nanoparticles. Not continuous coating.
- After oxidation, a superalloy is created on the surface of more basic alloys.

- Minimox® is a trademark of Material Interface, Inc.

Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Technical Benefits

- After thermal processing, yields a low surface energy coating.
- Creates a thin, robust surface modified layer.
- High temperature stable. Temperature limits imposed by alloy, not the coating process.
- Inside and outside surfaces can be treated – dipping or spraying application.
- Suspended nanoparticles. No VOC. Non-hazardous. pH 7. Surfactant is present.

Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Historical Development

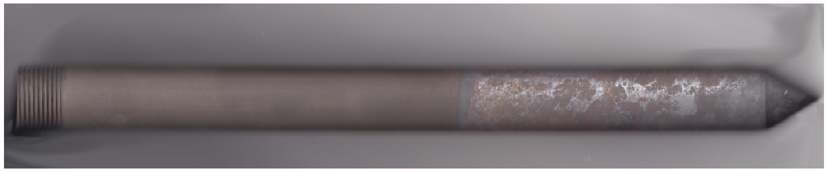
- Process created to improve high temperature oxidation.
- High temperature alloys contain rare earths for stable oxide layers.
- Water-based nanoparticles applied to surface have the same effect as rare earths added to the alloy, at significant cost savings.
- For oxidation resistance, good efficacy on stainless steel, nickel, aluminum, magnesium, and titanium alloys.

Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Oxidation Resistance Examples

Simple processing –
Amazing results

Thermocouple protection tube
304 stainless
200 hrs; 1500°F (815°C)



Treated - Thin, adherent oxide

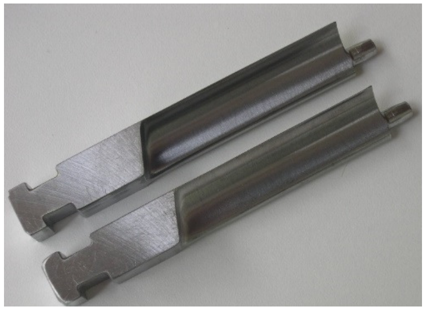
Untreated - Flaking non-protective oxide

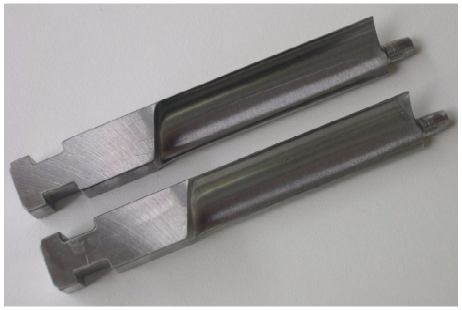
Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Oxidation Resistance Examples

Turbine Blade Heat Treating – 403 SS, Air, 1850°F (1010°C)

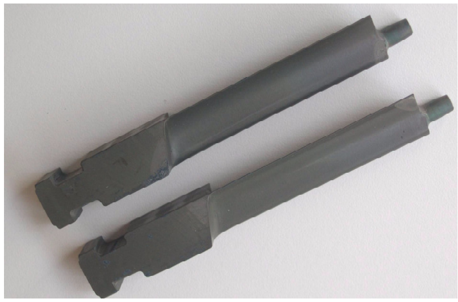
As-received





After Nano rare earth coating

Heat treated in air without rare earths

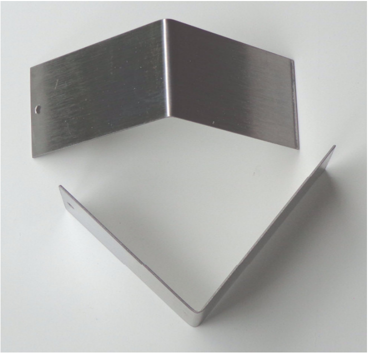
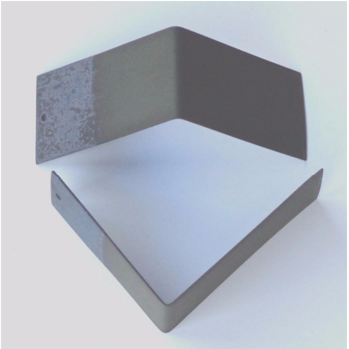


Heat treated in air with RE pretreatment

Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Durable

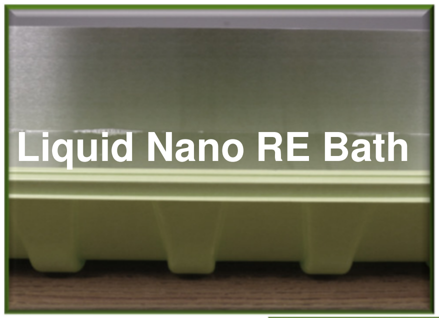
Coat flat stock; air dry	Bend	Successful protection

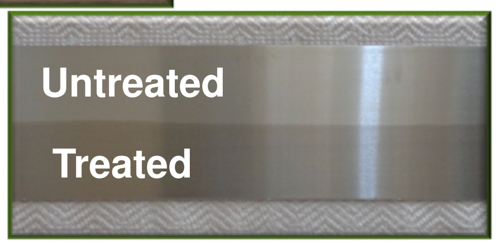




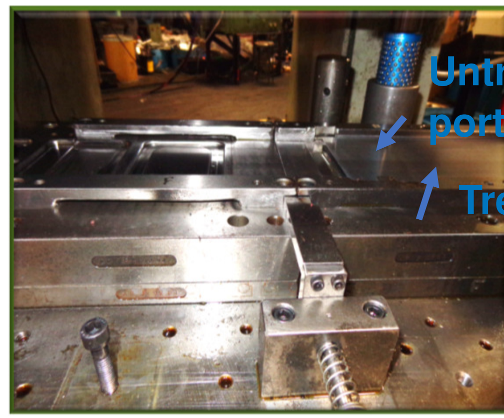
Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Durable

Coat flat stock; air dry	Stamping – no special handling





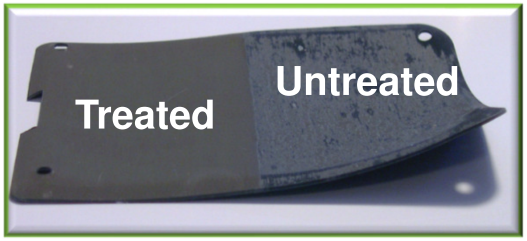


Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Durable

Successful protection –
No warping or deformation on treated side

1037°C (1900°F), 3 hrs



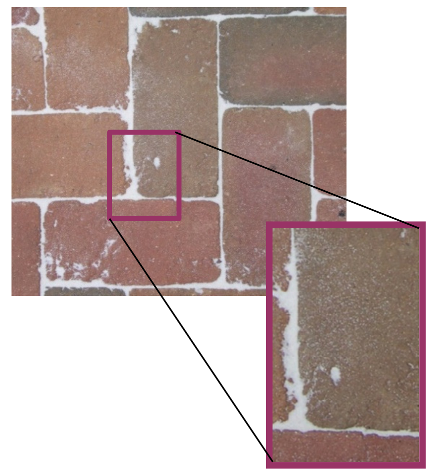
Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Different surface compounds

Untreated	Treated
410 Stainless, 850°C, 30 hrs	

Hydrophobic Coatings in Process Equipment

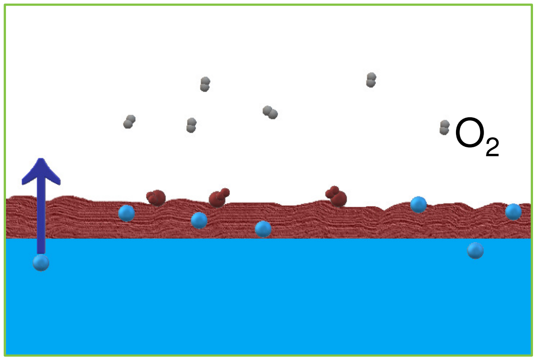
Rare Earth Coating – Different surface compounds – How?

Uncoated	Coated with large particles	Coated with discrete nanoparticles
		

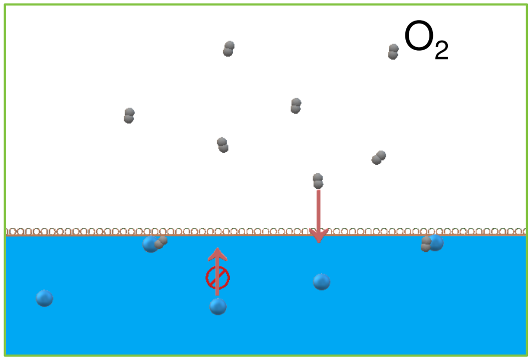
Nanoparticles fill in defects, grain boundaries, and alloy with the surface. Larger particles cannot do this.

Hydrophobic Coatings in Process Equipment

Rare Earth Coating – Different surface compounds – How?



Oxidation without Rare Earths
Metal diffuses through surface layer to react with oxygen



Oxidation with Rare Earths
Oxygen diffuses through surface layer to form oxide

Presence of rare earths –

- Changes direction of oxide layer formation
- Keeps the rare earths on the surface of the alloy
- Effectively halts diffusion in/out

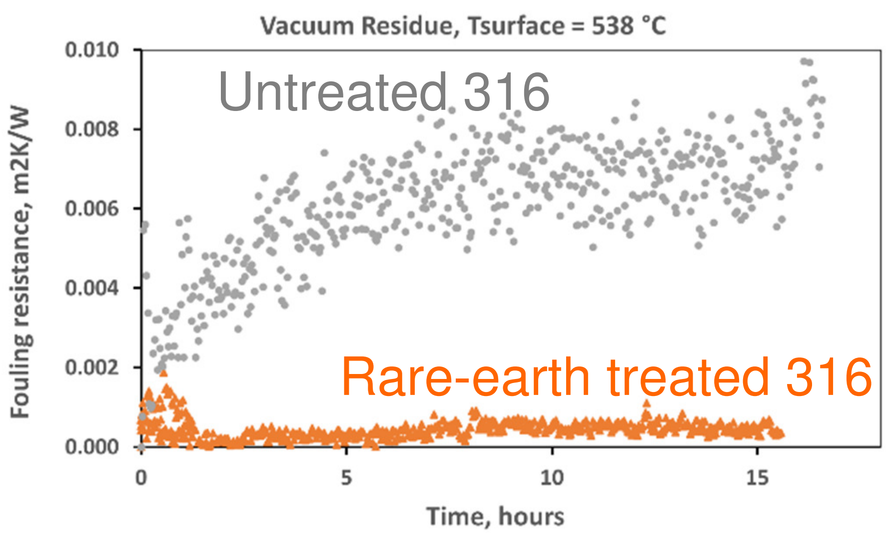
Hydrophobic Coatings in Process Equipment

Initial tests at Chevron (538°C, 1000°F) indicated rare earth coatings:

- Reduced fouling by 80% in laboratory test rigs
- Reduced adhesion of coke to the test sample

a. Untreated 316

b. Rare-earth treated 316



Hydrophobic Coatings in Process Equipment

Rare Earth Coatings

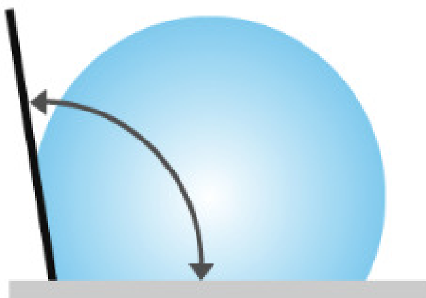
Initial tests at Chevron indicated rare earth coatings reduced fouling in laboratory test rigs.

Why?

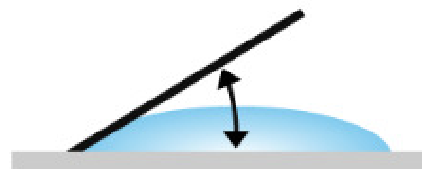
Surface energy measurements indicated the treated areas were hydrophobic. Is this the reason for reduced fouling? What other parameters may be relevant?

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Surface energy measurements



HIGH CONTACT ANGLE
Low surface energy,
Good release, non-stick properties
HYDROPHOBIC



LOW CONTACT ANGLE
High surface energy,
Poor release, Poor non-stick properties
HYDROPHILIC

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Multiyear Research Project

Matrix of alloys tested:
Nickel Alloy 200 (UNS N02200), Hastelloy C276 (UNS N10276)
304, 316, 317, 347, and 410 Stainless Steels,
Inconel 800 (UNS N08800), Inconel 825 (UNS N08825), Duplex 2205 (UNS S32305)
F5 (UNS K41545), F9 (UNS K90941), Titanium Grade 2 (UNS R50400) , 1008 carbon steel, aluminum bronze (UNS C95400).

Surface energy measured as a function of post-coating processing time and temperature. Also SEM/EDS and XPS.

System used for most of the surface energy measurements was a Krüss MSA (Mobile Surface Analyzer). Experiments verified with a Ramé-Hart Model 590 automated tensiometer at Chevron/Richmond.

Hydrophobic Coatings in Process Equipment

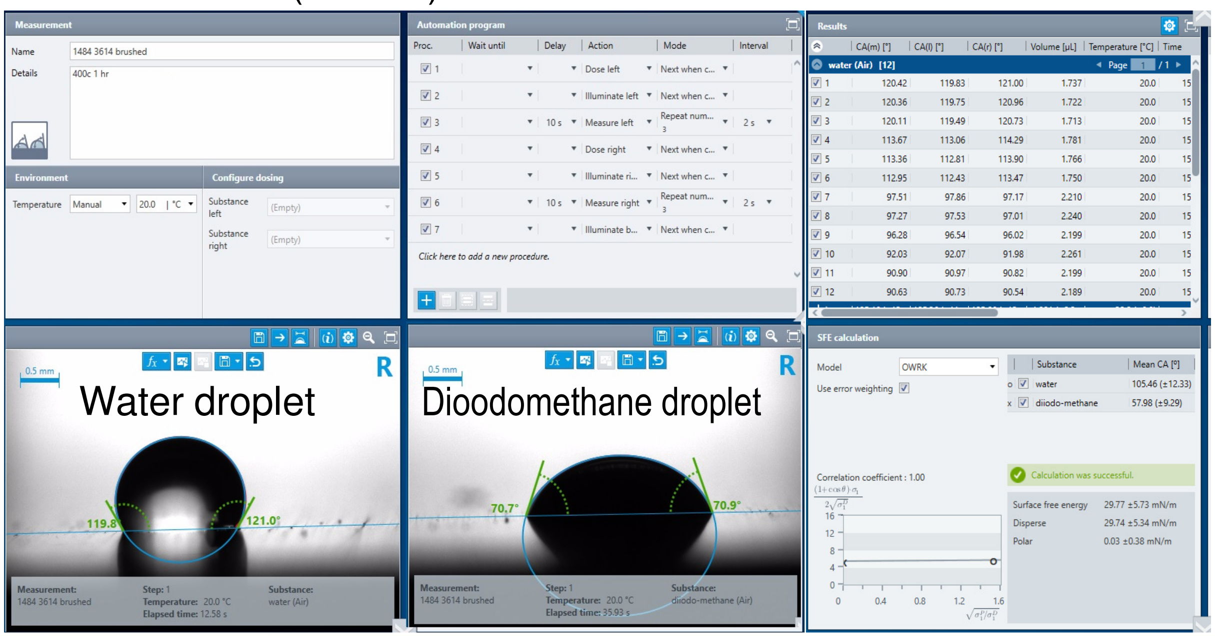
Rare Earth Coatings – Surface energy measurements

Automatically doses with water and diiodomethane droplets

Hydrophobic Coatings in Process Equipment

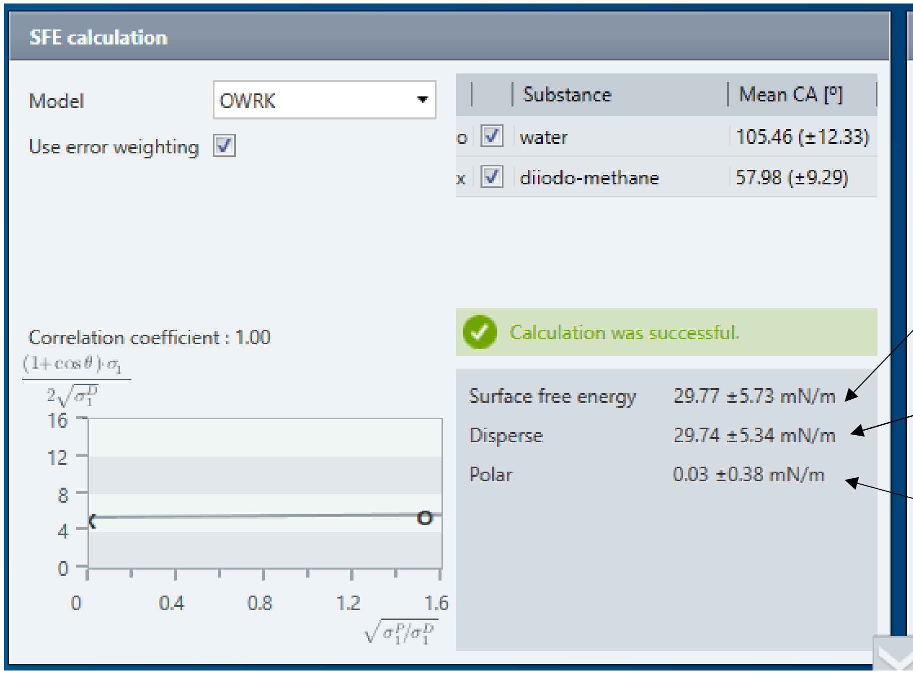
Rare Earth Coatings – Krüss MSA & Software

The MSA doses two parallel drops, followed by the direct analysis of the contact angles and the derived results of the surface free energy. The specific mathematical correction program is that of Owens-Wendt-Rabel-Kaelble (OWRK).



Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Krüss MSA & Software



The MSA software yields the total Surface Free Energy (SFE) and also the Disperse and Polar portions.

Total SFE = Disperse + Polar fractions

Disperse – Weaker van der Waals bonds.

Polar – Tight chemical bonds to adherents.

% Surface Polarity = Polar fraction/total SFE

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Multiyear Research Project

Surface energy measured f(post-coating time/temperature) for wide range of alloys.

Total SFE and % surface polarity measured.

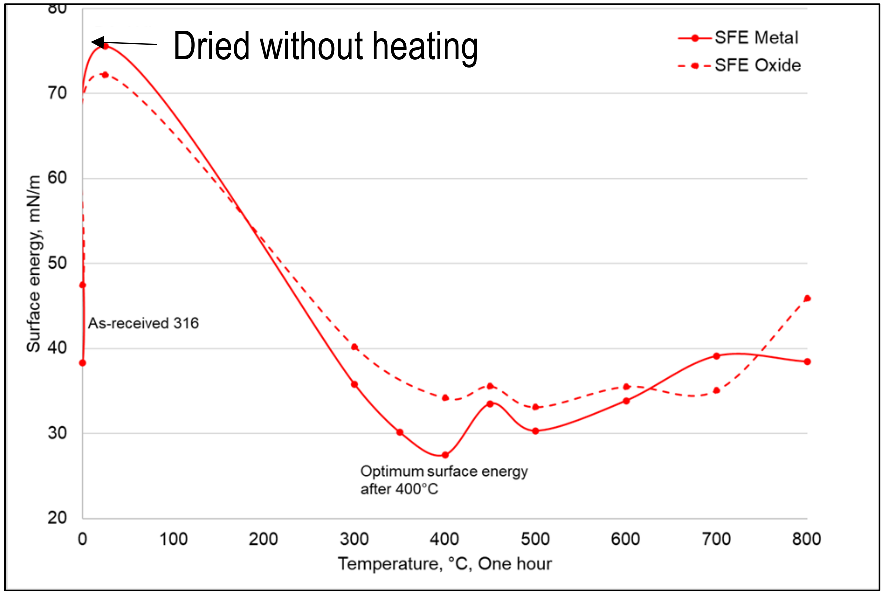
Test coupons usually had a mill oxide surface and a ground metallic surface on the reverse side.

What is in the coating? Generally Y_2O_3 and a surfactant.

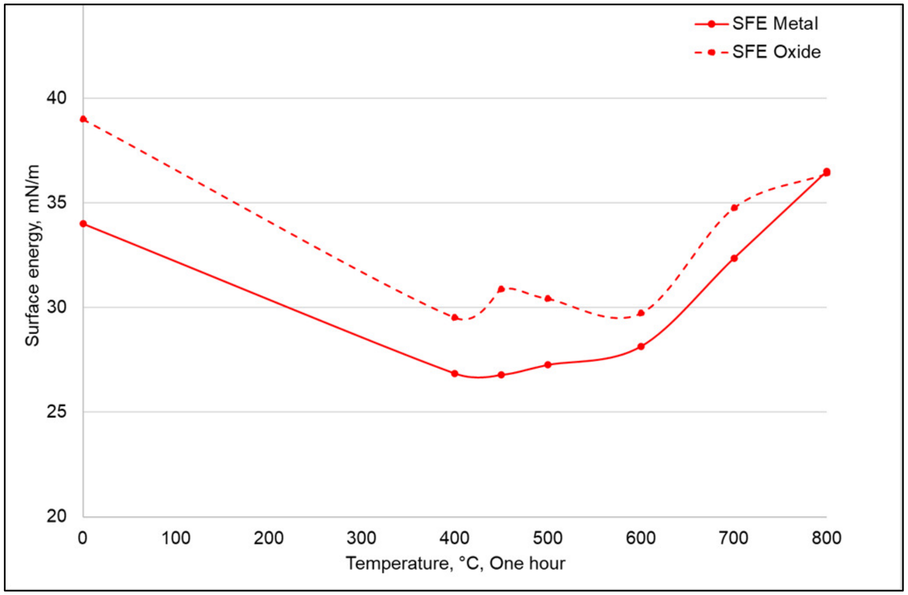
Hydrophobic Coatings in Process Equipment

Finding: Rare earth coatings reduce surface energy

SFE vs. Temperature, Alloy 316, Rare earth treated



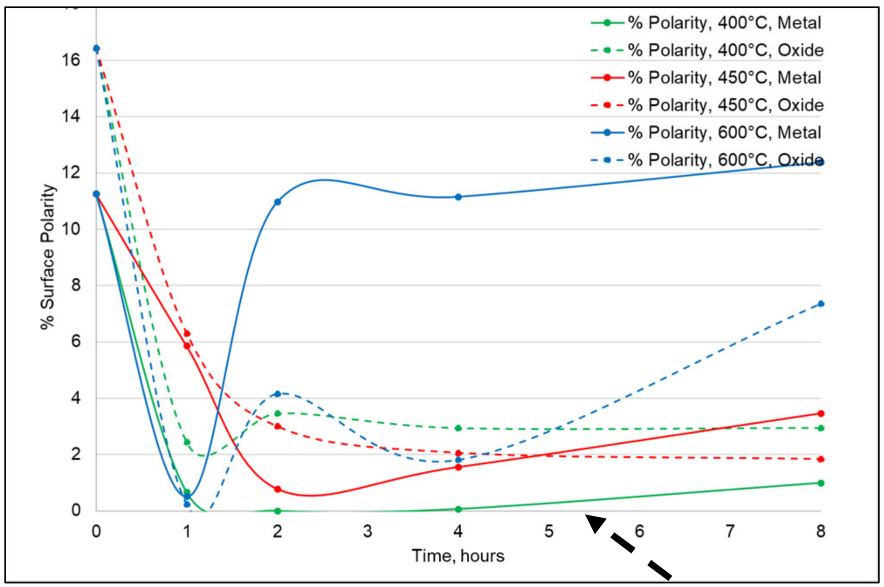
SFE vs. Temperature, Alloy 200, Rare earth treated



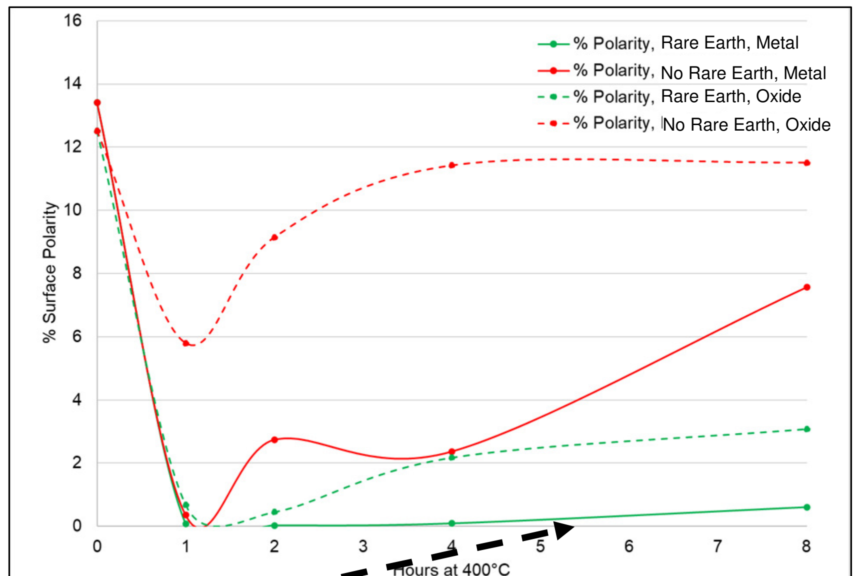
Hydrophobic Coatings in Process Equipment

Finding: Rare earth coatings reduce surface polarity to near 0%

% SP vs. Time &Temperature, Alloy 316,
Rare earth treated



%SP vs. Time, Alloy 200, 400°C
Rare earth treated vs. untreated

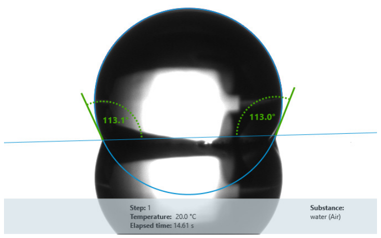


Low % surface polarity

Hydrophobic Coatings in Process Equipment

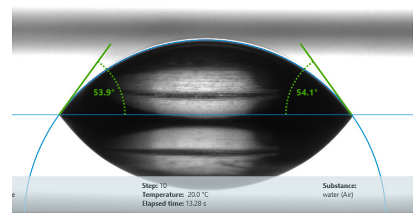
Rare Earth Coatings – Multiyear Research Project

316 stainless (mill oxide finish), Rare earth treated



Water contact angle = 113°
Surface energy = 26.4 mN/m;
% Surface polarity = 0.0%

316 stainless (mill oxide finish), Untreated



Water contact angle = 54°
Surface energy = 49.6 mN/m;
% Surface polarity = 22.1%

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Multiyear Research Project

Key Conclusions

- Essentially all alloys showed a minimum surface energy after processing to 400°C for one hour.
- F5 and F9 more difficult, but ultimately successful.
- Carbon steel also successful.
- *After heating to 400°C for one hour, the surface polarity approaches 0%.* The treated surfaces become nonpolar.

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Multiyear Research Project

- What is special about 400°C?
  - The surfactant burns off and a thin thermal oxide is grown
- What is special about Y_2O_3?
  - Surface energy is intrinsically related to a material's work function. The work function of Y_2O_3 is very low.
  - Catalytic activity?
- How thick is the thermal oxide + Y_2O_3?
  - About 100 nm

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Multiyear Research Project

What do the samples look like? Thin gold thermal oxide is present.
QC conducted with x-ray fluorescence (XRF) for yttrium.

(More obvious differences in previous slides at higher temperatures/long time.)

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Ramifications for Process Equipment

Because the layer is thin and integral to the alloy, it cannot spall/flake off.

Because it is thin, there is negligible additional thermal resistance associated with the treatment.

The surface layer cannot flake off with thermal cycling or bending.

The process is high-temperature stable and does not impose any temperature limitations beyond those of the base metal.

Surfaces generated are nonpolar.

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Ramifications for Process Equipment

Coating complex structures

- Rare earth coating can be applied to tortuous & complicated geometries
- Can be applied to low-clearance surfaces and structures that are not generally amenable to coating with other traditional systems.
- Treated surface can later be bent and formed with no major restrictions

If it can be wetted with water, it can be treated.

Hydrophobic Coatings in Process Equipment

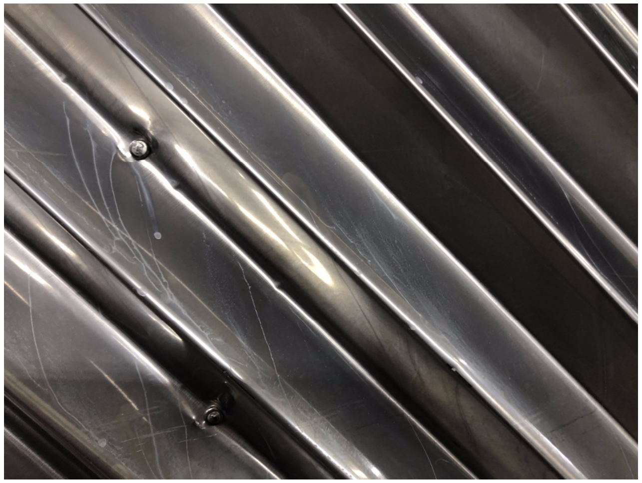
Rare Earth Coatings – Processing

Treated 317 stainless vacuum column wash bed

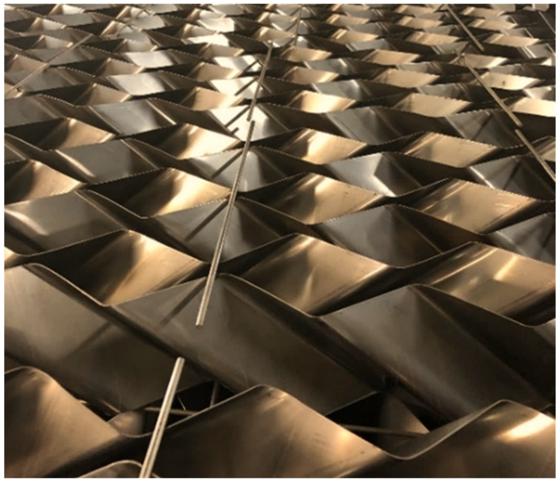
Two isopropanol wash tanks, blow off residues, dip in rare earth suspension, allow to drain, air dry, heat to 400°C for one hour.

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Vacuum Column Wash Bed



After dipping/air drying



After treatment + 400°

High surface area

In service for three years without showing any pressure drop buildup due to coking.

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Heat Exchangers

After treatment

Finned tubes

- Installed Summer 2022; expectations of improvement in ease of cleaning, thermal efficiency and reduction in fouling rates. Treated inside and outside tubing surfaces.

Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Heat Exchangers

Unexpected event caused rapid fouling. Removed after ≈ 6 mos.

Before cleaning

After cleaning 10,000 psig

Exchanger cleaned successfully with hydroblasting. Rare earths still present; reinstalled in service without recoating. Y_2O_3 verified still present with x-ray fluorescence.

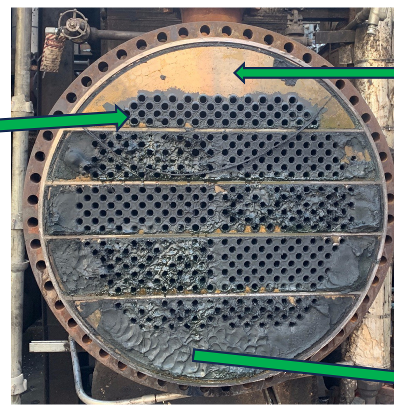
Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Heat Exchangers

Another unexpected event in same system again caused rapid fouling.

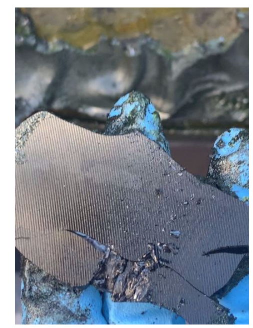
Tube sheet looked poor, but residue very loosely adhering.

2. Residue in tubes very friable and easily hydroblasted (10 sec)



1. Foulant fell off (hotter area)

3. Plastic scraper easily removed heavy foulant



Exchanger easily cleaned successfully with 12,500 psig hydroblast. Rare earths still present; reinstalled in service without recoating.

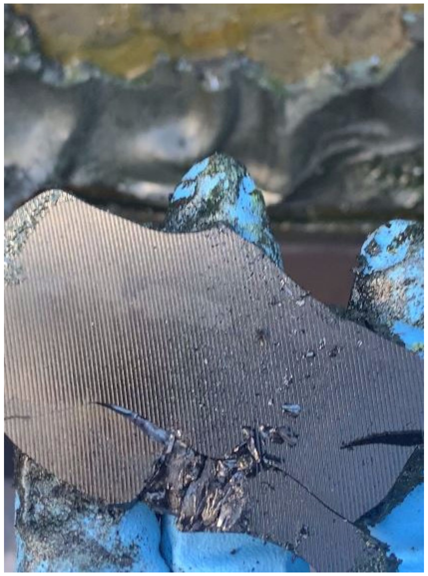
Hydrophobic Coatings in Process Equipment

Rare Earth Coatings – Heat Exchangers

Analysis of large foulant flake from tube sheet

Machining lines from tube sheet visible on foulant indicating clean separation.

FTIR indicated the surface against the tube sheet and the exposed surface contained identical organic species.
No yttria detected with XPS.



SURFACE FREE ENERGY (SFE) AND % SURFACE POLARITY OF SYSTEM:

Foulant in contact with tube sheet = 41 mN/m SFE, 0.4% polarity

Tube sheet = 24 mN/m SFE, 0.0% polarity

Two nonpolar surfaces in contact yield no adhesion.

Hydrophobic Coatings in Process Equipment

Value of Rare Earth Coatings Downstream Applications

- Reduced costs
  - Costs of fouling and decoking significantly lowered
  - Longer times between cleanings; easier cleaning
  - Still present after hydroblasting; no need to reapply
- Risk reduction
  - Fewer shutdowns
  - Lowers probability of safety incidents occurring

- Lowers production losses
  - Fewer unplanned shutdowns
- Better thermal efficiencies
  - Avoids thermal inefficiency
  - Reduced furnace firing
  - Less cooling needs
- Ability to process more challenging feedstocks
- Fine structures can be maintained (finned tubes, textured wash bed inserts)

Hydrophobic Coatings in Process Equipment

Off-shore, Subsea Processing Plants

Rare-earth coated stainless steel coupons were exposed to a salt-water-based subsea farm to determine the level of corrosion and bioadhesion.

- Rare-earth treated components showed less bioadhesion/corrosion than uncoated and Teflon-coated samples.
- Rare-earth coated aluminum bronze alloys, used in marine applications because of good mechanical properties and corrosion resistance, showed improved hydrophobicity and 0% surface polarity after treatment.
- Research on-going.

Hydrophobic Coatings in Process Equipment

Deployment

Production quantities available

International facilities for coating/heating/deployment

Hydrophobic Coatings in Process Equipment

Research and Development Team

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