2019 Award Nomination

Title of Innovation:

Volumetric Water Repellent Polyurethane Coating

Nominee(s)

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Category:

Coatings and Linings

Dates of Innovation Development:

(from [January, 2015] to [October, 2018])

Web site: www.hempel.com

Summary Description:

In the coatings industry, the development of a durable water repellent / superhydrophobic coating is of high interest to provide greater protection of steel structures from water, therefore reducing corrosion especially in severe offshore environments. This new coating actively repels water. We can demonstrate enhanced corrosion protection compared to conventional three coat systems used today, when the coating is used as part of a two coat system composed of the water repellent polyurethane with an activated epoxy zinc primer. The water resistance of the water repellent polyurethane was evaluated by salt spray tests on a direct to metal coating and the volumetric superhydrophobic effect can be seen by contact angle analyses. The results show a significant improvement in the water resistance and hence on the corrosion protection compared to standard coatings. The two coat system was compared to a standard three coat system in cyclic salt spray / QUV test; water condensation and ageing resistance test. The impact resistance and flexibility of the system were also tested. The two coat system has shown excellent anti-corrosive properties for extended times of

exposure and outstanding mechanical performance, making it a suitable candidate for areas exposed to aggressive environments such as offshore platforms.

The pictures below show a direct to metal salt spray test according to ISO9227 for a period of 1440 hours of the water repellent polyurethane at 120 microns or 5 mil dry film thickness against a standard polyurethane coating at the same dry film thickness. The water repellent polyurethane shows outstanding corrosion protection and creep resistance.

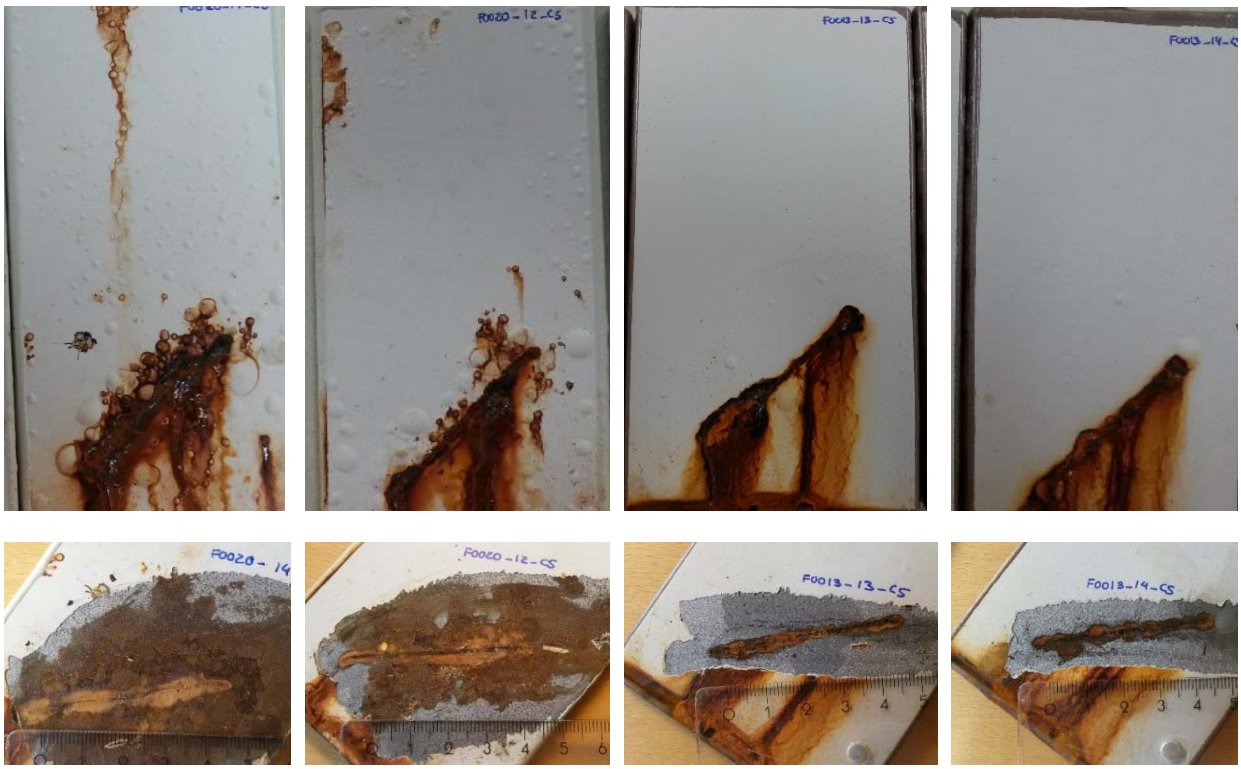


Photo 1. Left side: Standard polyurethane after 1440h of salt spray testing.
Right side: Water repellent polyurethane after 1440h of salt spray testing

Full Description:

1. What is the innovation?

We have developed the first coating that combats the two main coating failure mechanisms seen in severe environments: water ingress and micro cracking. This coating can be used for corrosion protection because it actively repels water from the coated surface; thus providing extended corrosion protection to steel in severe environments. The coating is based on a polyurethane binder system that has volumetric, but not surface superhydrophobicity, which provides active water repellency. This is combined with excellent mechanical robustness in terms of impact resistance, flexibility and thermal crack resistance. When used in combination with Hempel's patented Avantguard activated zinc primer, we have a two coat system that will offer longer lasting, superior protection to steel in severe environments compared to standard three coat systems used today.

2. How does the innovation work?

This innovation works for two reasons. Firstly the coating is built on a very flexible polyurethane backbone. This produces a very tough but flexible coating that prevents micro cracking and provides exceptional impact and thermal crack resistance. Cracking of organic coatings is one of the major mechanisms of coating failure as the coatings barrier properties are lost.

The water repellency depends on volumetric superhydrophobicity throughout the coating. Superhydrophobic surfaces are extremely difficult to wet with good examples seen in nature such as the lotus leaf. However, if the surface is damaged the superhydrophobicity is lost.

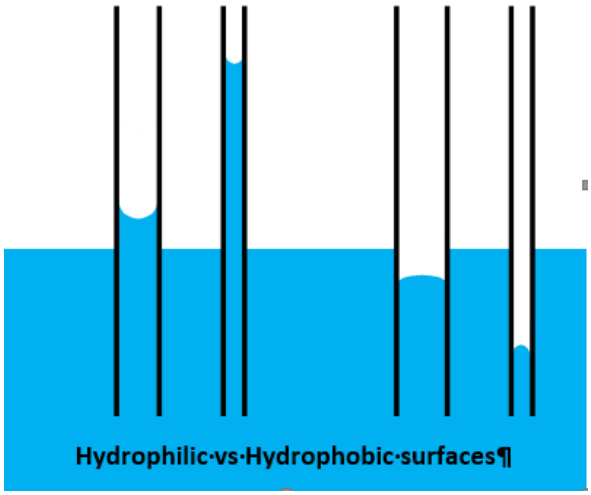


Figure 1. Capillary action. Hydrophilic versus hydrophobic. Capillary action.

This coating incorporates superhydrophobicity throughout the coating volume and creates a coating that does not rely on the surface property, but provides volumetric

superhydrophobicity that creates active water repellency. The coating is formulated above cPVC to utilize capillary forces to actively push water out of the coating.

The action of capillary forces is shown in the diagram in Figure 1. In the water repellent coating; the dry coating is porous and has a very large superhydrophobic surface area that actively pushes water out of the coating by the action of capillary forces. The adhesive force between the coating and the water is lower than the cohesive force in the water.

3. Describe the corrosion problem or technological gap that sparked the development of the innovation? How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

This technology has been designed to overcome the main industry challenges to coatings – water ingress and micro cracking. As water penetrates the film, the steel is no longer protected resulting in premature corrosion.

Coatings are generally designed to be barriers; to prevent water ingress through the film; but cannot stop water indefinitely. This technology relies on physics to actively repel water from the surface by creating a porous superhydrophobic network that actively pushes water out of the film. This is not a surface effect but a bulk effect; which makes the coating tough and durable and suitable for use in an oil and gas environment.

The other major failure mechanism is micro cracking. Cracked coatings can no longer act as barriers and failure occurs rapidly once the cracking has started. The water repellent coating is designed using a highly flexible but tough binder system that demonstrates superior impact resistance and flexibility. This also protects the coating from the effect of thermal cycling or stress.

This combination is ideal for a long life protective coating. The system is enhanced by utilizing Hempel's activated zinc primer technology which offers superior corrosion protection and improved mechanical properties compared to other zinc rich primers on the market.

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.

The main laboratory tests performed on the water repellent coating included:

A. Contact angle analyses;

B. Salt Spray Testing ISO 9227

For comparison, a standard polyurethane coating was also evaluated.

The main laboratory tests performed on the Water Repellent Polyurethane / Avantguard activated zinc rich epoxy primer system (Water Repellent System) included:

C. Cyclic corrosion according to ASTM D5894-16;

D. Ageing cyclic resistance according to ISO20340;

E. Continuous condensation according to ISO6270;

F. Impact resistance, flexibility and thermal crack resistance according to NACE TM0404

For comparison, a standard three coat system of activated zinc rich epoxy primer / epoxy intermediate / polyurethane topcoat (Standard System) was also evaluated.

Water Repellent Polyurethane testing

A. Contact Angle

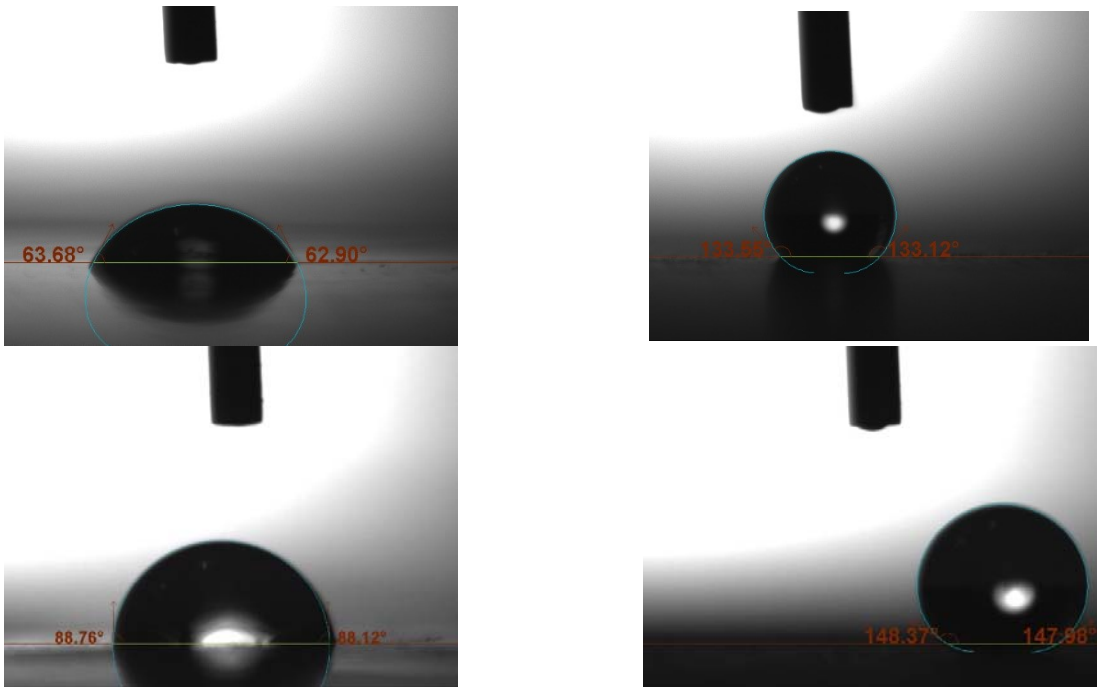
The apparent contact angles were measured using an Attension Theta Lite optical tensiometer; an apparatus consisting of a platform attached to a goniometer with a sample holder. The goniometer is calibrated using a levelling bubble in the base and is set to 180°. The apparatus also includes a device that holds a pipette at a measured distance from the platform on which the sample is placed. A microscope connected to a computer monitor is positioned in front of the goniometer platform and the platform is backlit. The coatings were applied on paper cards and the CA analysis were performed by cutting four 1X1 (in) squares, where three 4µL droplets were dropped and an image was taken. Image J software was used to determine the CA of the drop of water.

Contact angle analyses on the standard and water repellent polyurethane coatings were performed before and after abrading the coatings, using a 240 grit sand paper, in order to investigate the hydrophobic nature through the coating's volume. Averages of at least five different measurements were taken for each sample and the results are shown in Table 1. The standard showed a surface contact angle of 63,29° and a contact angle of 88,44°after it was sanded. The increase in contact angle values after the abrasion procedure can be justified by the increase of surface roughness after abrasion.

The surface contact angle values for water repellent polyurethane coating was 133,34°. After sanding, the contact angle increased dramatically to close to 150°C throughout the coating, indicating a volumetric superhydrophobic effect. The contact angles were consistent as the dry film thickness was reduced by sanding.

Table 1. Contact angle measurements for the coatings before and after sanding.

	Standard	**Water Repellent**
Surface	63,29°	133,34°
After sanding	88,44°	148,13°



Standard Polyurethane Water Repellent Polyurethane

Figure 2. Contact angle measurements for the coatings before (top) and after sanding (bottom).

B. Salt Spray Testing ISO9227

In order to evaluate the corrosion resistance of the polyurethane coatings; panels were exposed to SST according to ISO9227 for a period of 1440h and the results are shown in Table 2, Figure 3 and Figure 4 (best and worst results from each sample were chosen). After exposure, the degree of blistering, rust, cracking and flaking were assessed on both panel and around the scribe. Pull-off adhesion was evaluated 24h after the end of the test. The corrosion creep from the scribe was measured at least at nine points and the average width, M, was calculated according to Equation 1, where C is the average of the measurements and W is the original width of the scribe.

$$M = \frac{C-W}{2} \quad (1)$$

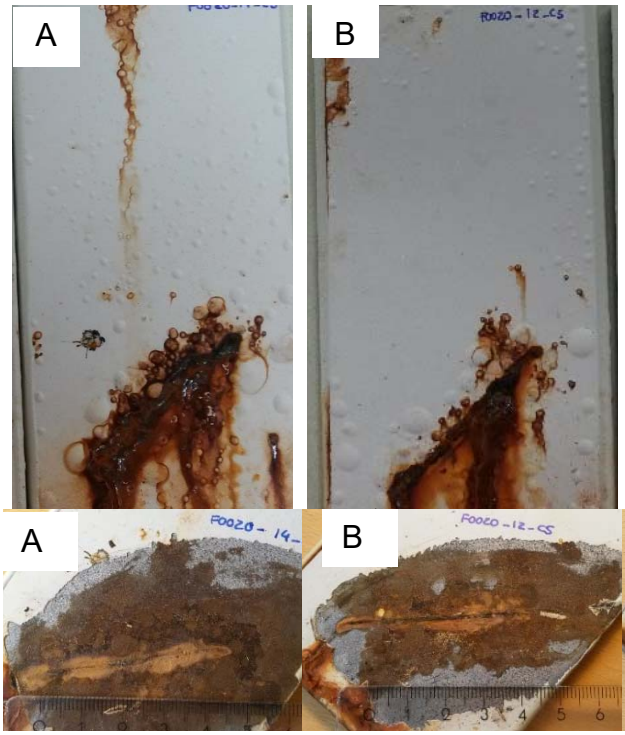


Figure 3. Pictures of Standard Polyurethane after 1440h of SST.

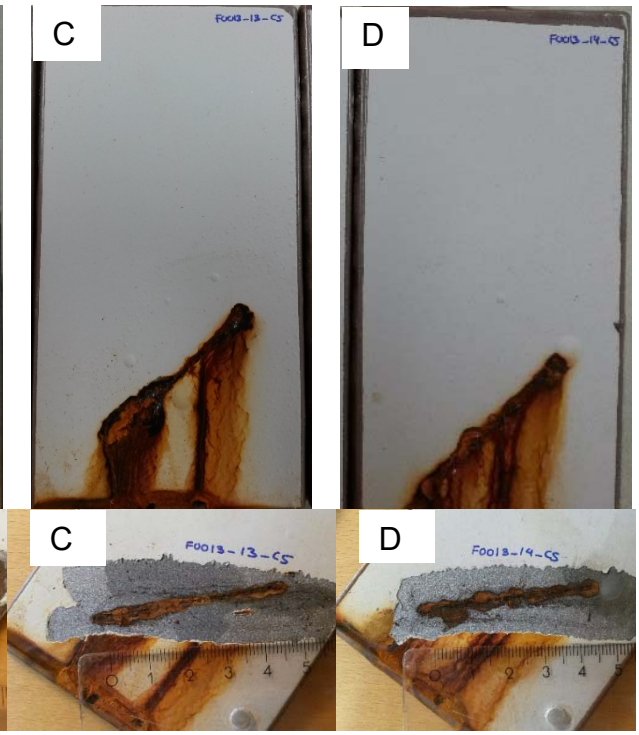


Figure 4. Pictures of Water Repellent Polyurethane after 1440h of SST.

Standard polyurethane coating showed a high degree of blistering, Figure 3; whereas, the sample with water repellent coating only shows a few blisters,Figure 4. Concerning the scribe line, it is possible to observe a considerable reduction in the rust area around the scribe for the water repellent coating. However, it should be noted that after 1440h of SST, tiny rust spots were observed under the coat in all the samples, indicating that moisture is able to penetrate the coatings after long exposure periods. The measurements of the creep line width for the different panels are summarized onTable 2.

Table 2. Creep line values, calculated according to Equation (1), for the different samples.

	Standard Polyurethane (120 µm)	**Water Repellent (120 µm)**
Creep line (mm), after SST exposure for 1440h	A) >> 5 B) >> 5	C) 1.5 D) 1.8

Water Repellent two coat system

C. Cyclic Corrosion testing ASTM D5894-16

Cyclic test results for a standard three coat system and the two coat water repellent system, exposed for 2016h; which is twice as long as a normal test; are shown on Table 3 below.
No visible defects were observed after the exposure times but the corrosion creep was significantly lower in the water repellent system compared to the standard system.

Table 3. Panels evaluation after ASTM D5894-16, after 2016 hours of exposure.

System	Standard system	Two coat water repellent system
DFT (µm)	Primer: 60 Intermediate: 160 Topcoat: 60	Primer: 80 Topcoat: 200
Time of Exposure: 2016 hours		
Average of corrosion line, M, (mm)Average	M = 2,1	M = 0,2

D. Ageing cyclic resistance according to ISO20340

The standard three coat system and the two coat water repellent system were compared on the ageing cycling resistance test over the standard exposure time of 4200 hours. The two coat water repellent system was further tested over extended periods of time to include, 7200 and 10080 hours. The creep results are shown in Table 4 and Table 5 below, and the results are shown in summary in Figure 5. No blistering, cracking, flaking, rust or any other visible defect after the exposure times were observed. Both system meet the criteria of ISO 20340 and corrosion creep is less than 3 mm for both systems. It is important to note the loss of adhesion in the standard system compared to the retention of adhesion in the water repellent system.

As the test duration is extended the corrosion creep increases; as would be expected. Nevertheless, the panels retained good appearance and most importantly adhesion was retained during the extended exposure.

Table 4. Panels evaluation after ageing cycling resistance test according to ISO 20340.

System	Standard System	Water Repellent System
DFT (µm)	Primer: 60 Intermediate: 160 Topcoat: 60	Primer: 80 Topcoat: 200
Time of Exposure: 4200 h		
Observations	Blistering:0(S0), Rusting: Ri0, Flaking: 0(S0), Cracking: 0(S0)	
Creep (mm)	2,8	2,2
Adhesion (MPa) (type of fracture)	11,7 (B)	5,5 (A/B)
Adhesion (MPa) reference (type of fracture)	17,3 (C/D)	7,9 (C)

Type of fracture according to ISO 4624:

A/B	Fracture between the steel and first coat	(Adhesion failure)
B	Fracture in the first coat	(Cohesion failure)
B/C	Fracture between the first and second coat	(Adhesion failure)
C	Fracture in the second coat	(Cohesion failure)
C/D	Fracture between the second and third coat	(Adhesion failure)
D	Fracture in the third coat	(Cohesion failure)

Table 5. Panels evaluation after extended ageing cycling resistance test according to ISO 20340.

System	**Water Repellent System**		
DFT (µm)	Primer: 140 Topcoat: 140		
	Time of Exposure (h)		
	4200	7200	10800
Observations	Blistering:0(S0), Rusting: Ri0, Flaking: 0(S0), Cracking: 0(S0)		
Creep (mm)	2.1	5.3	6.8
Adhesion MPa	6.8 (C)	6.8 (C)	6.7 (C)
Adhesion MPa reference	6.9 (C)		

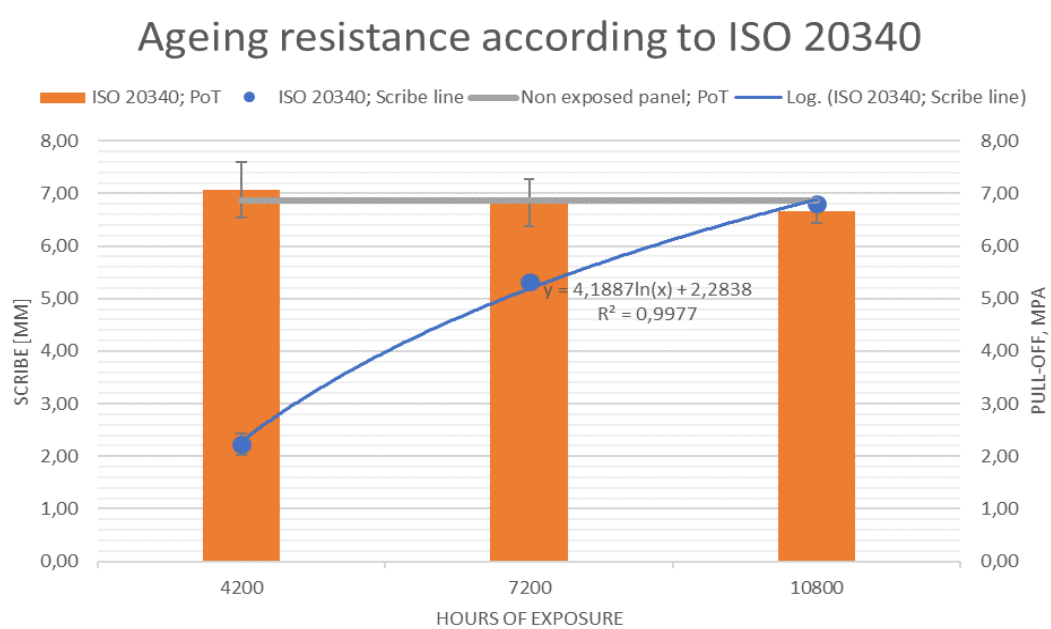


Figure 5. Ageing Cycling Resistance Test of the water repellent system - results for rust creep and adhesion.

E. Continuous condensation according to ISO 6270

After 720h of continuous condensation test exposure, both the water repellent system and the standard system showed no signs of blistering, rusting, flaking or cracking, Table 6 below. The water repellent system showed a 92% retention of the POT adhesion value when compared to the reference, while the Standard had only 42% POT adhesion retention.

Table 6. Panels evaluation after continuous condensation for 720h.

System	Standard System	Water Repellent System
DFT (µm)	Primer: 60 Intermediate: 160 Topcoat: 60	Primer: 80 Topcoat: 200
Observations	Blistering:0(S0), Rusting: Ri0 Flaking: 0(S0), Cracking: 0(S0)	Blistering: 0(S0), Rusting: Ri0 Flaking: 0(S0), Cracking: 0(S0)
Pull-off Adhesion Average (MPa)	5.6	6.0
Pull-off Adhesion Reference (MPa)	13.2	6.5
Adhesion Failure Mode	C (intermediate)	C (topcoat)

F. Impact, flexibility and thermal crack resistance according to NACE TM0404-2004

Impact Resistance and Flexibility of the water repellent system and the Standard system were performed according NACE TM0404, Section 13 and 12 at room temperature (23°C/73°F) and low temperature (-5°C/23°F).

The test panels were only coated on one side of the steel panels with the standard system and the water repellent system; then cured for 2 weeks at room temperature. After this time, the test specimens were post cured at 60°C for one week and the respective flexure strain was measured using a fixed-radii mandrel bending machine.

The flexure strain, F_{strain}, of the coating systems material were calculated using the equation:

$$F_{strain}=\frac{\frac{t}{2}+c}{R+\frac{t}{2}} \quad (2)$$

t = steel panel thickness; c = coating system thickness; R = mandrel radius (mm). The deformed coatings were evaluated visually and microscopically for signs of cracking.

The results are shown in Table 7. The water repellent system shows excellent flexibility even at low temperature and impact resistance is retained at low temperature compared to the standard system. Post testing salt fog exposure showed no rust formation on the water repellent test panels while the standard showed rust at the damaged area of the panel.

Table 7. Impact, flexibility and thermal crack resistance results.

	Standard System	**Water Repellent System**
Flexibility RT [%]	1.5 / crack	3.1/ No crack
Flexibility (-5°C/23°F) [%]	0.8/ crack	3.0/ No crack
Impact resistance– RT [J]	4.9	4.9
Impact resistance (-5°C/23°F) [J]	3.1	4.3
Post-SST	Rust-Reported	No rust
Thermal crack resistance (1x DFT)	No cracks	No cracks
Thermal crack resistance (2x DFT)	No cracks	No cracks
Thermal crack resistance (3x DFT)	Cracks	No cracks

5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?

This new technology allows the use of a two coat system to replace a conventional three coat system that is predominately in use today. The system consists of two products which will be available globally:

- ✓ Hempadur Avantguard 770: SSPC Paint 20, Type 2, Level 2 and compliant to ISO20340, Norsok M501, revision 6 in a coating scheme.
- ✓ Water Repellent Polyurethane topcoat.

Products are applicable with standard application equipment used today in both new building and maintenance. Productivity is greatly enhance by the ability to eliminate one coat from the system and the primer can be overcoated after 2 hours to allow completion of an area in one day.

The improved corrosion protection shown by the water repellent system coupled with the improved mechanical properties will result in a longer service life of assets.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?

The primer used in the system, Hempadur Avantguard 770 has been available commercially since September 2014. The water repellent polyurethane is currently being field tested in the

Gulf of Mexico, Australia, Colombia and United Kingdom. Further field trials are planned to take place over the next 12 months. Full product launch is anticipated in 2019.

The main challenge is managing change in a conservative world. Changing outside of the conventional standards will require continued testing both in the laboratory and real world while managing applications to reassure customers that the system is both easy to use and longer lasting.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

Title: Anti-corrosive zinc primer coating compositions comprising hollow glass spheres and a conductive pigment.

Patent No.: WO2014/032844

Inventors: Colominas Tutusaus, Salvador; Santiago Colodar, Arias; Schandel, Torben; Redondo, Tomás Alhambra; Paulsen, Andreas Lundtang.