Challenging the Performance of Inorganic Zinc Rich vs Organic Zinc Rich Primers and Activated Zinc Technology

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Abstract

Activated zinc technology combines galvanic, barrier and inhibition mechanisms in the protection of steel and, as such, it significantly reduces the effect of corrosion stress. Primers based on this technology increase durability, improve mechanical properties, enlarge the application window and therefore increase productivity. This has been proven in extensive tests against state-of-the-art standard zinc primers, actually used in the field.

Zinc rich primer coatings, both organic and inorganic, are extensively used in highly corrosive environments and they are an integral part of a high-performance coating system in the Protective Coatings Industry. During the 60's and the 70's, zinc rich epoxy primers dominated the market. Later, zinc ethyl silicate primers took over this role, but nowadays it appears as if zinc epoxy primers have made a comeback. Some of the advantages of zinc epoxies compared to zinc silicates are the less demanding curing conditions (epoxies will cure at low humidity), they are easier to overcoat and they are less demanding to substrate preparation prior to application. Zinc rich epoxies are typically formulated with high levels of zinc dust and the epoxies are mechanically stronger than silicates meaning that over thickness is less problematic for new generation of activated zinc epoxies than for zinc silicates that can fail by mud cracking. According to ISO 12944 a zinc rich coating contains more than 80% zinc by weight in the dry film.

In studies made at Hempel and presented at NACE in 2007 it was shown that only about one third of the zinc particles in zinc rich epoxies are utilised for galvanic protection of the steel. This finding was the starting point to develop a new technology that would increase zinc activation.

The protecting mechanism of zinc rich coatings is believed mainly to be based on galvanic protection provided by the zinc dust in the paint. When a coating system containing a zinc, rich primer is exposed to a corrosive environment, rust creep and blistering are amongst the most important failure mechanisms to be considered. Many accelerated exposures will not, within their exposure time, show the defects visually on intact coated surfaces. Therefore, behaviour of the coatings involving artificially made damages, i.e., scores, are given significant considerations in the development of efficient anti-corrosive primers. Many prequalification tests (e.g. ISO 12944-6[1], ISO 20340[2], NORSOK M501 Rev.6[3]) are based amongst others on rust creep and blistering as well as detachment from scores.

The increasing demands on the performance of zinc rich primers (low rust creep and better mechanical properties) has focussed attention on maximizing the utilization of the zinc dust in the paint. In addition to this, the recent developments in the market prices of zinc dust suggest opportunities for new developments in this area. Is it now possible to achieve the same level of corrosion protection with an organic binder containing the same level of zinc dust as its inorganic equivalent? Previously Zinc rich epoxy coatings required higher levels of zinc dust to achieve the same level of corrosion protection as their inorganic zinc silicate counterparts.

All these benefits can be achieved with innovative, activated zinc rich epoxies which are specifically designed to provide extreme corrosion protection, durability, productivity and improved mechanical performance.

The purpose of this paper is to describe the protecting mechanisms of a new generation of zinc rich primers with enhanced protection vs organic and inorganic zinc rich primers. The performance properties of the new generation primer have been proven with real results from different corrosion tests (ISO 12944-6, Salt Spray Test according to ISO 9227[4], NACE Cracking Test TM0304[5]) vs inorganic zinc rich primers which will be presented as well.

Keywords: "Zinc epoxy", "active fillers", "Corrosion Protection", "Rust Creep", "Zinc silicate", "activated zinc"

Introduction

Zinc rich primers, both organic and in-organic coatings, are extensively used in the marine and offshore industry. The beneficial effect of zinc rich primer on the longevity of protective coatings is primarily assumed to be due to a cathodic protection mechanism. During the 60's and the 70's zinc rich epoxy primers dominated the market. Later, zinc ethyl silicate primers took over mainly due to their higher potential to corrosion protection. Today, new developments in activated zinc epoxy primers are setting the two categories of Zinc rich primers on the same level in terms of anticorrosion performance [6].

Some of the advantages of zinc epoxies compared to zinc silicates are the less demanding curing conditions (epoxies will cure faster regardless of the humidity level), they are easier to overcoat (the porosity of silicates may cause popping), they are less demanding to substrate preparation prior to application and they have lower VOC content. Furthermore, zinc silicates will have a tendency to mud cracking even at moderate film thickness [7]. This makes the zinc epoxy primers very attractive for maintenance use and for new building where surface preparation and application requirements cannot be met; when ease of application is required and/or where climate conditions during application do not favour zinc silicates [8].

The increasing demands on the performance of zinc rich primers (low rust creep) has generated even more focus on maximizing the utilization of the zinc dust in the paint and optimizing the rust creep resistance [9].

In zinc rich primers, zinc is used as a pigment to produce an anodic active coating. Zinc will sacrifice itself and protect the steel substrate which becomes the cathode. The resistance to corrosion is dependent on the transfer of galvanic current by the zinc primer. As long as the conductivity in the system is preserved and there is sufficient zinc to act as anode the steel will be protected galvanically. Therefore, zinc pigment particles in zinc primers are packed closely together and they are typically formulated with very high loadings of zinc dust. However, barrier effects and inhibitive protection effects are also provided by the zinc corrosion products, known as "post-cathodic protection" [10].

The demands on protective coatings used in offshore environment are very high and modern paint systems are so durable that upon exposure to natural weathering they may show little signs of deterioration. If an anticorrosive coating system remains intact during its service life it may; for the best systems; maintain protection for up to 15-20 years with minimal maintenance. The use of new technologies and paint formulations means that new coatings are used with little or no previous track record. This has resulted in more emphasis being placed on accelerated laboratory testing to evaluate coating performance. Many of these accelerated exposure tests will not, within their exposure time show the negative effects visually on intact coated surfaces. Therefore behaviour of the coatings around artificially made damages i.e. scores are given significant considerations, and many prequalification tests are based amongst others on rust creep and blistering as well as detachment from scores: NORSOK M-501, ISO 20340, NACE TM0104[11], TM020412[12], TM0304, TM0404[13]. One of the requirements for prequalification of zinc primers according to ISO 20340 is rust creep below 3 mm (0,118 in).

The use of alloyed zinc has been described previously [14,15] as a possible way to improve the anticorrosive behaviour of zinc primers. The addition of small amounts of alloying metals to the zinc used in zinc epoxy and zinc silicate primers enhances the performance of these coatings.

The industry is looking to use the latest technologies available in order to reduce the associated maintenance and repairs cost that will arrive later. As well as systems that increase application productivity.
We have found all these benefits can be achieved and improved with a new innovative anti-corrosion technology, based on activated zinc.

This new technology, as we show in this paper, is innovative in the way it combines galvanic, barrier and inhibition mechanisms to achieve a still higher level of steel protection. As a result, we have developed a coating which significantly reduces the effect of corrosion stress, increasing durability and mechanical performance whilst increasing productivity. These improvements have been proved in extensive tests and compared against standard zinc primers, both organic and inorganic.

The developed solution is based on the combination of the elements used in traditional zinc epoxies with two new substances – hollow glass spheres and proprietary activators.
In addition to this, activated zinc coatings offer one more advantage when it comes to anti-corrosive protection: an increased scavenger, or inhibitor, effect. Over time, chloride ions penetrate protective coatings and cause pitting corrosion, especially in aggressive saltwater environments. Activated Zinc rich coatings capture chloride ions by forming chloride-containing salts around the glass spheres. This significantly delays the corrosive process as the chloride ions are trapped in the coating and cannot reach the surface of the steel.

Zinc rich epoxies are often used in applications that expose the steel to severe mechanical stress, such as extreme temperature fluctuations found in some industries and environments. However, in a typical zinc protective system, the zinc primer is the weakest mechanical point. As a result, cracks can form in the coating as the steel expands and contracts. Activated zinc coatings are different due to an added self-healing capability.

This high performance has been achieved as a result of two processes: the ability of hollow glass spheres to stop cracks and a positive effect that results from the unique zinc activation process.
The purpose of this paper is to describe the protecting mechanisms of this new generation of activated zinc rich epoxy primers with enhanced protection vs inorganic zinc rich primers. The performance properties of the new generation primer have been proven with results from different standard corrosion tests (ISO 12944-6, Salt Spray Test according to ISO 9227, NACE Cracking Test TM0304…) and benchmarked against inorganic zinc rich primers, results which will be presented as well.

Experimental procedure

Exposure Testing according to ISO 20340

Procedure A: Standard procedure with low temperature exposure (thermal shock). The exposure cycle used in this procedure lasts a full week (168 hours) and includes 72 hours of QUV Accelerated Weathering Tester, 72 hours of Salt Spray test (SST) and 24 hours of thermal shock (-20°C; -4°F)
The QUV exposure is according to ISO 11507, accelerated weathering, by exposure to fluorescent ultraviolet (UV) light and condensation in order to simulate the deterioration caused by sunlight and water as rain or dew. UV cycle: 4 hours UV-light at 60±3°C (140°F) with UVA-340 lamps and 4 hours condensation at 50±3°C (122°F).

The SST exposure is according to ISO 9227, exposure to constant spray with 5% NaCl solution at 35°C (95°F). The thermal shock exposure consists of placing the panels in a freezer, at -20±2°C.

Total period of exposure: 25 cycles equal to 4200 hours. Before the panels are started in the climatic cycle, they are given a 2 mm (0.079 in) wide score placed horizontally, 20 mm (0.79 in) from the bottom and sides. When the test is stopped, the paint film is removed from the score, and the width of the rusting is evaluated.

After removing the coating by a suitable method, the width of the corrosion is measured at nine points (the midpoint of the scribe line and four other points, S mm apart, on each side of the midpoint).

The rust creep M is calculated from the equation

$M = (C - W)/2$ (1), where C is the average of the nine width measurements and W is the original width of the scribe.

Salt Spray Test (SST), according to ISO 9227, neutral salt spray.

This method is performed in order to evaluate the corrosion resistance of a coating system by reproducing the corrosion that occurs in atmosphere containing salt spray or splash.

The operation conditions of the salt spray test are constant spray with 5% NaCl solution at 35°C.

After ending of the exposure, blistering and rust are evaluated on both panel and around the score (in mm from centre), according to ISO 4628-2 and ISO 4628-3, respectively. Cracking is evaluated according to ISO 4628-4[16]. Adhesion is evaluated according ISO 4624[17] (pull-off tests).

After removing the coating at the score by a suitable method (mechanical or chemical cleaning), the width of the corrosion is measured at nine points. The rust creep M is calculated from the equation $M = (C - W)/2$, where C is the average of the nine width measurements and W is the original width of the scribe (0.5 mm / 0.020 in).

Thermal cycling resistance test

The thermal cycling test (TCT) is carried out according to the NACE standard TM0304. Coated U-panels (the standard calls them C-channel blocks) are exposed to thermal cycles consisting of cooling to -30°C (-22°F) for 1 hour followed by heating to +60°C (140°F) for 1 hour. The panels are inspected after 252 cycles (3 weeks).

Flexibility Test

Flexibility test according to NACE standard TM0304 consists on the application of one side of 6 panels at the specified DFT. Panels are post cured at 60ºC (140ºF) for one week in addition to the initial curing at room temperature for one week. To measure the flexure strain of the coating a fixed-radii mandrel bending machine. The bare of the test panel is bent over the fixed-radius steel mandrel. The deformed coating surface has to be examined for signs of cracking using a microscope and a low voltage holiday detector. If no cracking then the test is repeated with a smaller radius. The process should be repeated until cracking is detected.

Impact Resistance test

Flexibility test according to NACE standard TM0304 consists on the application of one side of steel panels at the specified DFT. Panels are post cured at 60ºC (140ºF) for one week in addition

to the initial curing at room temperature for one week. Test in conducted in accordance with procedures described in ASTM G 14[18] and D 2794[19].

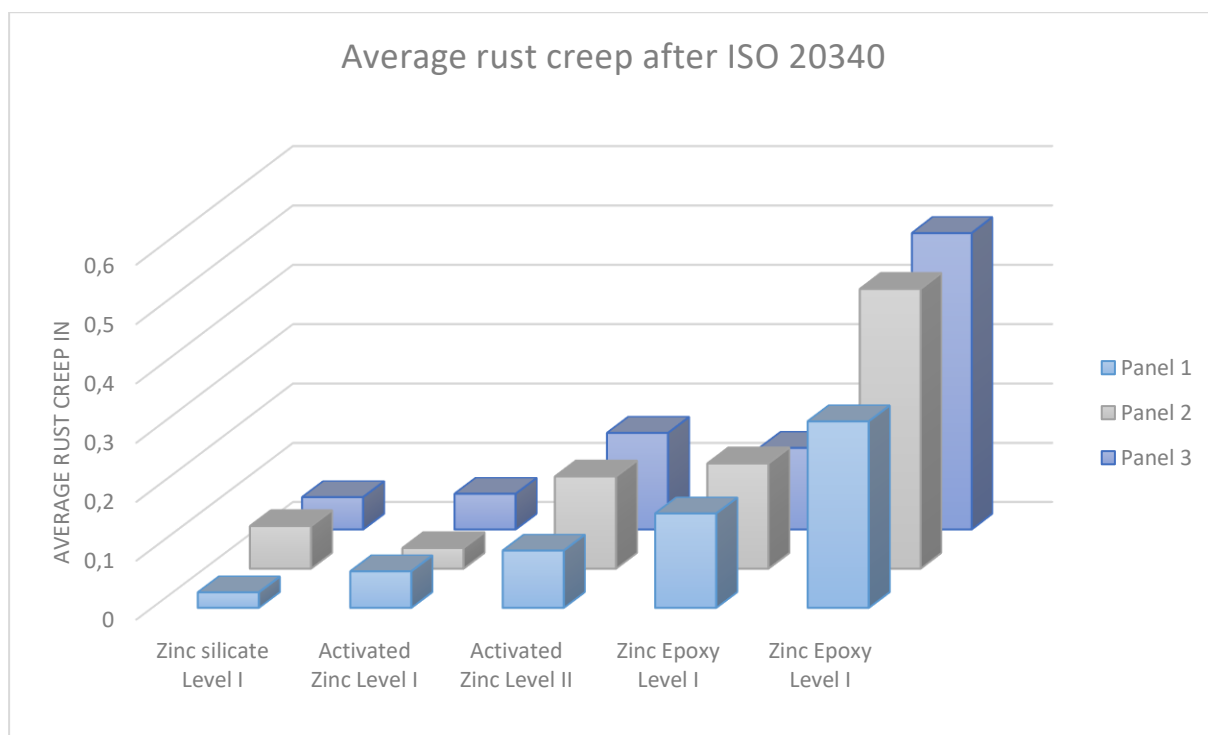## **Results and conclusions**

Results according to ISO 20340

Figure 1: Tests done on steel panels coated 60 µm (2.4 mils) of primer + 160 µm (6.4 mils) of epoxy midcoat + 60 µm (2.4 mils) of aliphatic polyurethane topcoat. The steel panels (7.5 cm x 15 cm x 0.5 cm; 2.96 x 5.91 x 0.197 in) are cold rolled mild steel, abrasive blasted to Sa2 ½ (ISO 8501-1[21]), with a surface profile equivalent to BN 10 (Medium)

Table 1
Photographs after evaluation in ISO 20340

Full coating system (Primer + Epoxy midcoat + Polyurethane topcoat)				
Std. Zinc epoxy technology		Activated zinc technology SSPC type 2 Level II	Zinc Silicate SSPC type 1 Level I	Activated zinc technology SSPC type 2 Level I
SSPC type 2 Level I	SSPC type 2 Level I			

Note: Coating system based on 60µm (2.4 mils) of primer + 160µm (6.4 mils) of midcoat + 60 µm (2.4 mils) of topcoat

After 6 months of cycle exposure according to ISO 20340 (72h exposure to QUV-A, 72h exposure to Salt Spray and 24h exposure to -20ºC/-4ºF), rust creep of new zinc epoxy technology level I is on par with IOZ (Inorganic Zinc Silicate level I) and much better than products with Std. Technology level I.

Results according to ISO 9227, neutral salt spray.
Primers

Table 2
Photographs after evaluation in ISO 9227

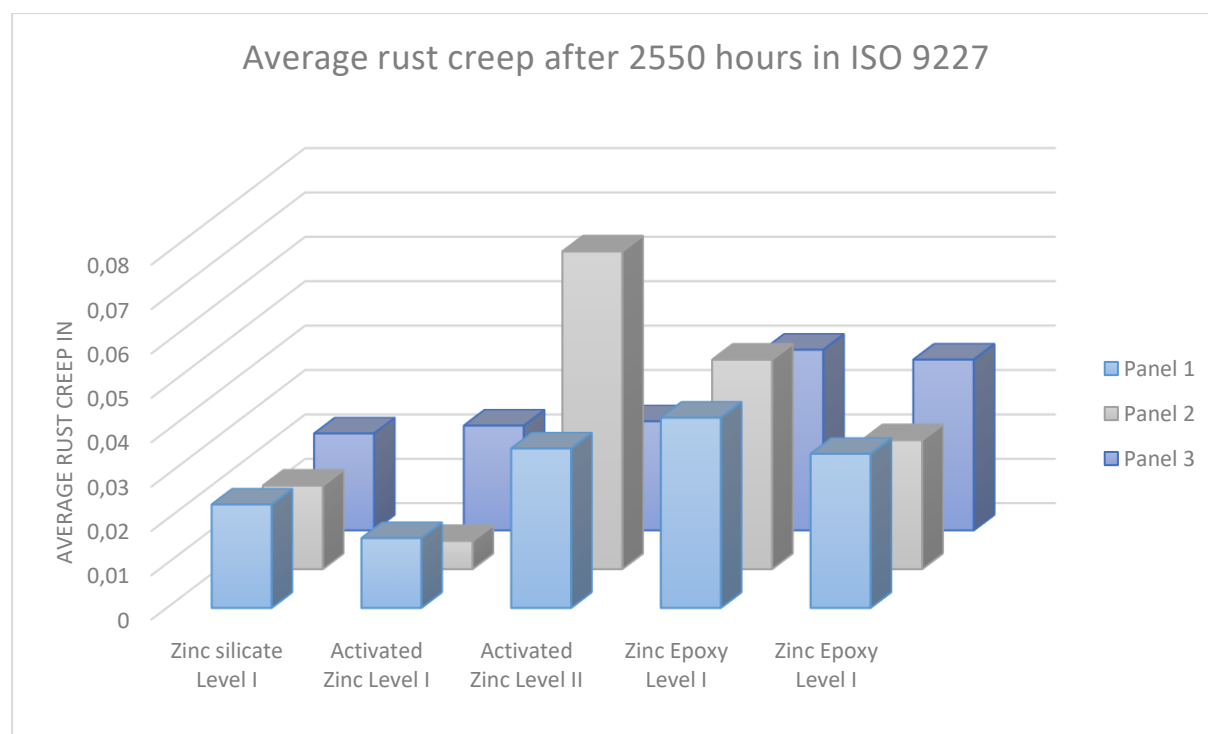| After 8 months (5760h) in Salt Spray exposure				
Std. Zinc epoxy technology		Activated zinc technology SSPC type 2 Level II	Zinc silicate SSPC type 1 Level I	Activated zinc technology SSPC type 2 Level I
SSPC type 2 Level I	SSPC type 2 Level I			
Note: Tests done on steel panels coated with 1x60 µm (2.4mils) of the paint tested				

Results after 2550 hours (3 coats system)

Figure 2: Tests done on steel panels coated 60 µm (2.4 mils) of primer + 160 µm (6.4 mils) of epoxy midcoat + 60 µm (2.4 mils) of aliphatic polyurethane topcoat. The steel panels (7.5 cm

x 15 cm x 0.5 cm; 2.96 x 5.91 x 0.197 in) are cold rolled mild steel, abrasive blasted to Sa2 1/2 (ISO 8501-1), with a surface profile equivalent to BN 10 (Medium)

Table 3
Photographs after evaluation in ISO 9227

Full coating system (Primer + Epoxy midcoat + Polyurethane topcoat)				
Std. Zinc epoxy technology		Activated zinc technology SSPC type 2 Level II	Zinc silicate SSPC type 1 Level I	Activated zinc technology SSPC type 2 Level I
SSPC type 2 Level I	SSPC type 2 Level I			

Note: Coating system based on 60µm (2.4 mils) of Zn primer + 160µm (6.4 mils) of midcoat + 60 µm (2.4 mils) of topcoat

After 2550 hours the new Activated zinc level I product and IOZ level I show very low rust creep and less rust creep than standard epoxy primers level I of zinc level and activated zinc with 80% Zn. New Activated zinc level I product performs on slightly better than IOZ level I.
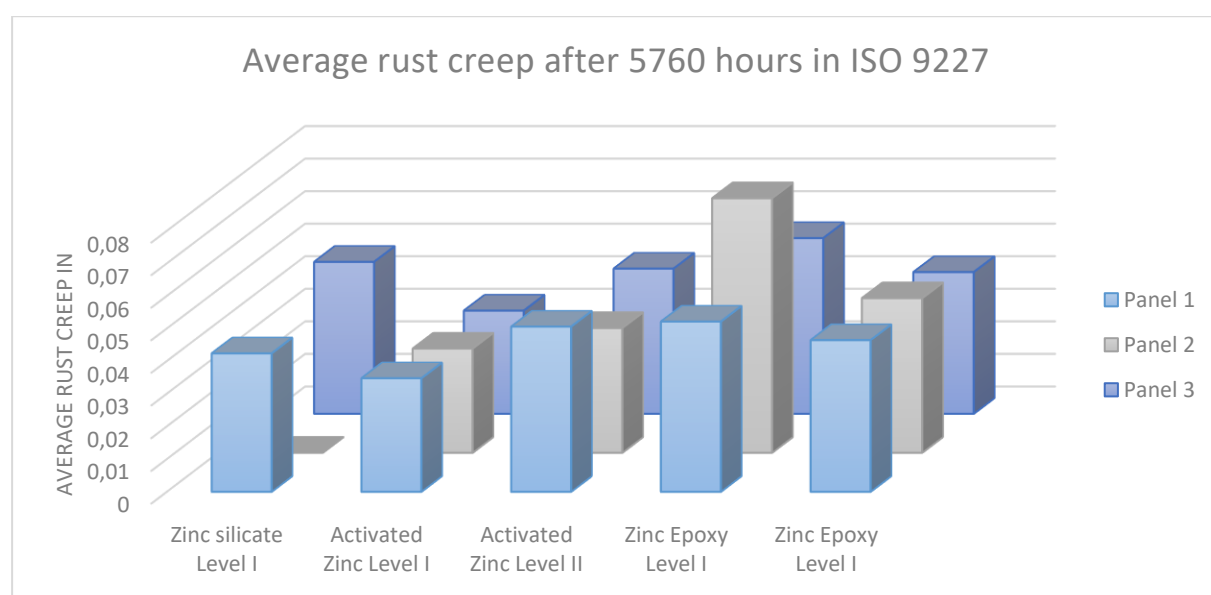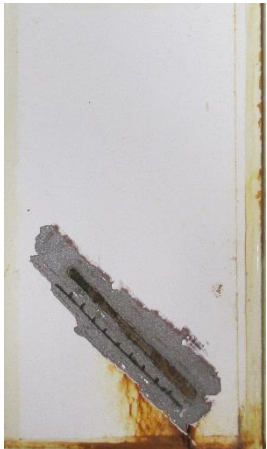
Results after 5760 hours (3 coats system)

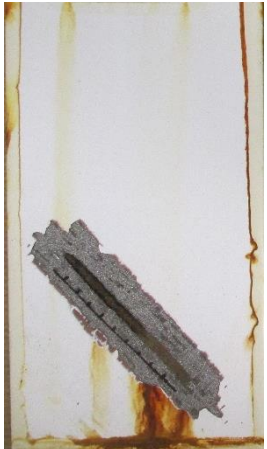Average rust creep after 5760 hours in ISO 9227

Figure 3: Tests done on steel panels coated 60 µm (2.4 mils) of primer + 160 µm (6.4 mils) of epoxy midcoat + 60 µm (2.4 mils) of aliphatic polyurethane topcoat. The steel panels (7.5 cm x 15 cm x 0.5 cm; 2.96 x 5.91 x 0.197 in) are cold rolled mild steel, abrasive blasted to Sa2 1/2 (ISO 8501-1), with a surface profile equivalent to BN 10 (Medium)

Table 4
Photographs after evaluation in ISO 9227

Full coating system (Primer + Epoxy midcoat + Polyurethane topcoat)				
Std. Zinc epoxy technology		Activated zinc technology SSPC type 2 Level II	Zinc silicate SSPC type 1 Level I	Activated zinc technology SSPC type 2 Level I
SSPC type 2 Level I	SSPC type 2 Level I			

Note: Coating system based on 60µm (2.4 mils) of Zn primer + 160µm (6.4 mils) of midcoat + 60 µm (2.4 mils) of topcoat

After 5760 hours the new Activated zinc level I product and IOZ level I show very low rust creep. New Activated zinc product performs on slightly better than IOZ.

Results of Thermal cycling resistance test according to NACE standard TM0304

Three coats system based on Zinc primer + Epoxy midcoat + PUR. Products are applied at specified thickness and 3 times more than specified thickness.

Table 5
Results of cracking test

Panel No.	Primer	DFT of the system	Naked eye	Under x 20 zoom
15 A	AVG Level I	247,5 µm (9,9 mil)	No Visible Cracks	No Visible Cracks
16 A	AVG Level I	234,8 µm (9.4 mil)	No Visible Cracks	No Visible Cracks
19 A	IOZ level I	313,4 µm (12,5 mil)	No Visible Cracks	No Visible Cracks
20 A	IOZ level I	330,2 µm (13,2 mil)	No Visible Cracks	No Visible Cracks

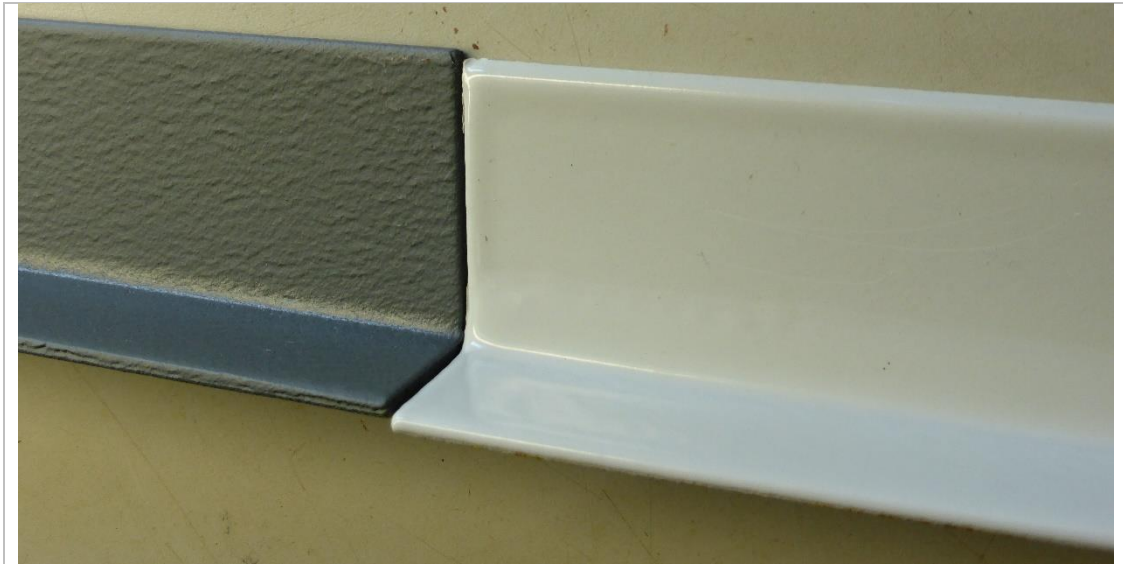|				
15 B	AVG Level I	887,6 µm (35,5 mil)	No Visible Cracks	No Visible Cracks
16 B	AVG Level I	931,2 µm (37,2 mil)	No Visible Cracks	No Visible Cracks
19 B	IOZ Level I	Cracked	Not Exposed	
20 B	IOZ Level I	Cracked	Not Exposed	

Figure 4: L-Panels with Epoxy Activated Zinc

One coat primer. Products are applied at 3 and 4 times more than specified thickness.

Table 6
Results of cracking test

Panel No.	Primer	DFT	Naked eye
21	AVG Level I	171,7 µm (6,9 mil)	No Visible Cracks
22	AVG Level I	163,3 µm (6,5 mil)	No Visible Cracks
23	AVG Level I	235,1 µm (9,4 mil)	No Visible Cracks
24	AVG Level I	252 µm (10,1 mil)	No Visible Cracks
25	AVG Level I	280,8 µm (11,2 mil)	No Visible Cracks
26	AVG Level I	256,6 µm (10,3 mil)	No Visible Cracks
33	IOZ Level I	Cracked	Not Exposed
34	IOZ Level I	Cracked	Not Exposed
35	IOZ Level I	Cracked	Not Exposed
36	IOZ Level I	Cracked	Not Exposed
37	IOZ Level I	Cracked	Not Exposed

| 38 | IOZ Level I | Cracked | Not Exposed |

Using NACE std. test method, it is demonstrated that the Activated Zinc Technology Level I performs better than Std. Technology and IOZ Level I. According to both tests Activated zinc can resist 3-4 times the specified DFT value without cracking.

Flexibility Test Results

Only primers at specified thickness.

Table 7
Results of flexibility test

Panel no.	System	Mandrel Radius(mm)	Mandrel Radius(inches)	Total DFT (µm)	Total DFT (mils)	Flexure strain (e)	Flexure strain (%e)
60		38,5	1,5	77	3,1	0,0394	3,94
61		70,5	2,8	78,5	3,1	0,0219	2,19
62	AVG Level I	58,5	2,3	71,5	2,9	0,0262	2,62
63		58,5	2,3	82,4	3,3	0,0264	2,64
64		58,5	2,3	87	3,5	0,0265	2,65
65		58,5	2,3	91,7	3,7	0,0265	2,65
				Average			2,78
72		58,5	2,3	88,7	3,5	0,0265	2,65
73		70,5	2,8	88,2	3,5	0,0221	2,21
74	IOZ Level I	58,5	2,3	82,4	3,3	0,0264	2,64
75		70,5	2,8	67,7	2,7	0,0218	2,18
76		58,5	2,3	88,3	3,5	0,0265	2,65
77		58,5	2,3	77,6	3,1	0,0263	2,63
				Average			2,49

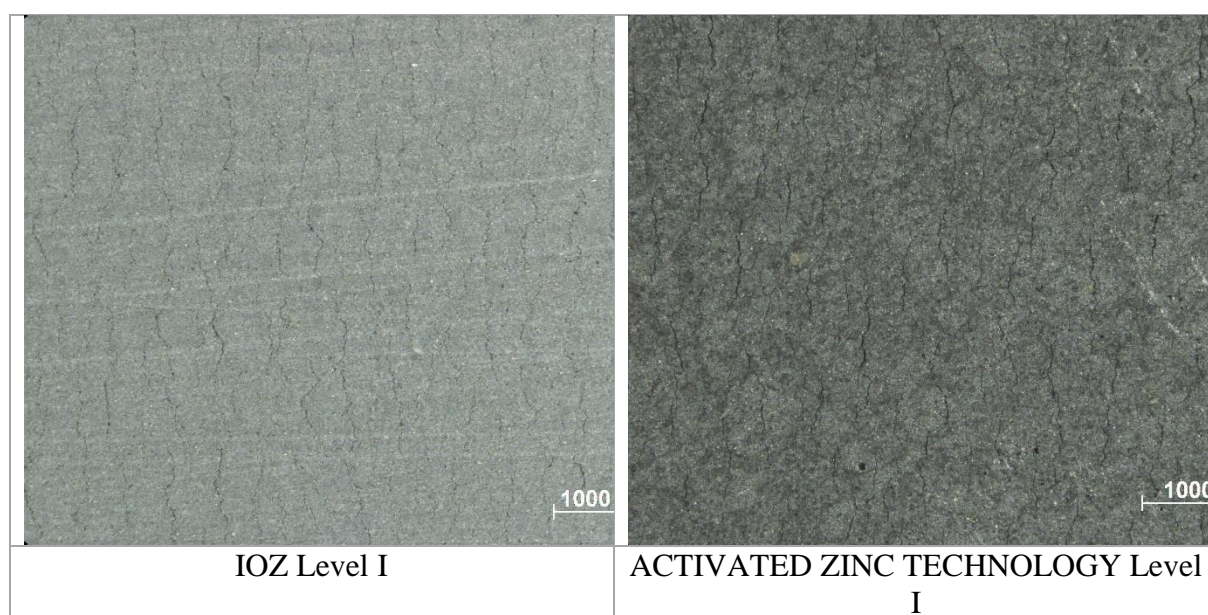| IOZ Level I | ACTIVATED ZINC TECHNOLOGY Level I |

Figure 5: Results of flexibility test

Activated zinc technology Level I shows slightly better flexibility than IOZ Level I when only primer is tested.

Impact Resistance test

Table 8
Results of impact test

Panel No.	System	Value in inch-pound	Value in Joule
78	Activated zinc Technology (3 coats system)	57	6,5
80	IOZ (3 coats system)	41	4,7
81	Activated zinc Technology	66	7,5
83	IOZ	41	4,7

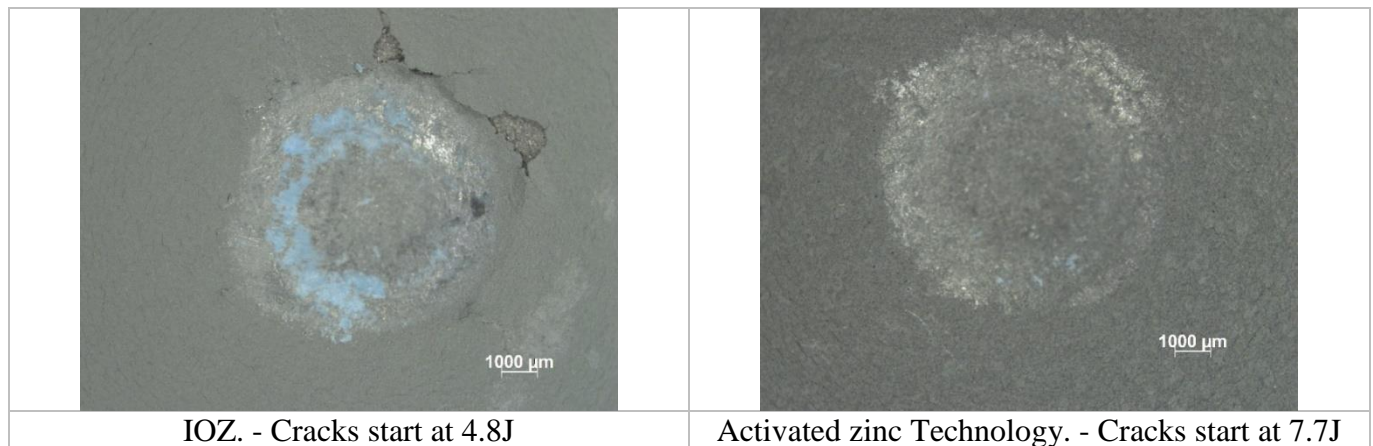| IOZ. - Cracks start at 4.8J | Activated zinc Technology. - Cracks start at 7.7J |

Figure 6: Results of impact test

Activated zinc technology shows higher impact resistance (around 60% more) than IOZ.

Conclusions

After 6 months of cyclic exposure according to ISO 20340,the rust creep of new activated zinc epoxy technology level I is on par with IOZ (Inorganic Zinc Silicate) Level I and much better than conventional zinc rich epoxies.

After 2550 hours of salt spray according to ISO12944 the new Activated zinc product and IOZ pass the test with a very low rust creep. The new activated zinc epoxy product performs on slightly better than inorganic zinc silicate.

After 5760 hours of salt spray the new activated zinc rich epoxy product and inorganic zinc silicate show very low rust creep. The new activated zinc rich epoxy product performs slightly better than the inorganic zinc silicate.

Using the NACE standard TM0404 it is demonstrated that the activated zinc rich epoxy technology, Level I, performs better than conventional zinc rich epoxy technology and inorganic zinc silicates. According to both tests the activated zinc rich epoxy is able to resist 3-4 times the specified DFT value without cracking.

Activated zinc rich epoxy technology shows slightly better flexibility than inorganic zinc silicate when only the primer is tested.

Activated zinc rich epoxy technology shows higher impact resistance (around 60% more) than inorganic zinc silicate.

Taking into account all these points it is proven that Activated zinc technology Level I could be a good alternative to Zn silicates and also to metallization in structures where resistance to high temperature (more than 160ºC/320ºF) is not required.

<u>Acknowledgements</u>

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