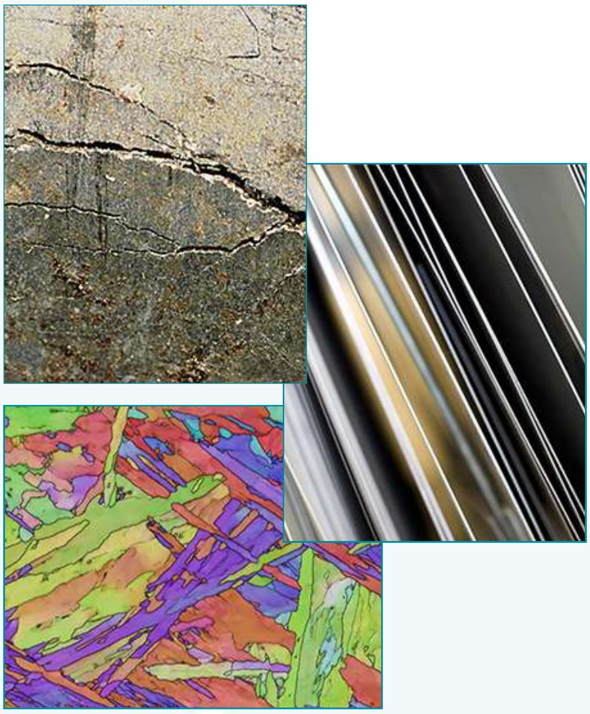

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Corrosion testing and electrochemical comparison of various alternative coatings

Björn Tidbeck, Alexi Makdesy, Viktor Fahlgren, Joachim Blomquist and Karin Beaussant Törne

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Abstract

In this study, ten different coating systems have been tested in accelerated corrosion tests and towards natural weathering at Bohus-Malmön. Most of the systems have also been evaluated by electrochemical measurements. The coating systems tested comprise alternative coating systems that do not meet the specifications in the general Swedish coating requirements in AMA-anläggning. The coating systems have been selected from a list of alternative systems that was compiled as a part of a literature study performed within MRC Corrosion protection The selected systems could potentially offer better solutions for protecting various assets in the industry and infrastructure. The tested single coat systems include: Zinga, ZingAlu, Fontezinc HR, EonCoat, Carboguard 858 and Carbozinc 11. The tested 3-coat systems include: A C5 Hempel 3-coat system based on Avantguard technology. A C5 Carboline 3-coat system based on Carboguard 858 and a C5 3-coat reference system with 90 % zinc according to AMA-Anläggning. The Zinga systems performed much better in the ISO 12944-9 test compared with the VDA test. Both Zinga coatings have very active pigmentation. Zinga require periods of dry conditions to perform optimally, in that sense, it behaves much like hot dip galvanizing. The performance of the 3-coat systems was similar. The AMA reference system was slightly better with regards to rusting at the scribe. Generally, the Norsok test appears somewhat more challenging to the 3-coat systems compared to the VDA test. The best performing coatings in the accelerated tests was a stand- alone zinc epoxy, Carboguard 858 and a waterborne zinc rich silicate, Fontezinc HR. The stand-alone zinc ethyl silicate, Carbozinc 11 performed better than the 3-coat systems. The complementing field exposure at Bohus-Malmön was started on the 9th of October 2018. After about 1,5 years, the ZingAlu samples have started to rust and the Eon Coat samples have started to flake with adhesive failure between the topcoat and the basecoat. Other than that, it is too early to draw any conclusions from the field exposure. Reoccurring ocular examination will be performed and reported yearly within MRC Corrosion Protection. The zinc pigmentation in zinc rich coatings behave differently depending on the coating vehicle and the pigmentation. In other words, the properties of the binder and/ or other additives can affect the electrochemical activity of the zinc pigment. There are several established mechanisms by which zinc rich coatings can protect steel, these include: Galvanic protection, Barrier protection, Inhibition of the steel. It is clear that the expression of these mechanisms can be tailored by choosing an appropriate binder, additives and degree of pigmentation. Depending on the exposure it is not always best to have an active zinc. Rather, the key to success appears to be a moderately active zinc pigmentation. The zinc activity can be controlled by: Inhibition of the zinc, Activation of the zinc, Electrically conductive additives and the Amount of pigmentation.

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1 Introduction

In this study, ten different coating systems have been tested in accelerated corrosion tests and towards natural weathering at Bohus-Malmön. Most of the systems have also been evaluated by electrochemical measurements. The coating systems tested comprise alternative coating systems that do not meet the specifications in the general Swedish coating requirements in AMA-anläggning. The coating systems covered in this study have been selected from a list of alternative systems that was compiled as a part of a literature study performed within MRC Corrosion protection [1]. The selected systems could potentially offer better solutions for protecting various assets in the industry and infrastructure. The potential benefits and a short description of each alternative coating system is described in section 2. This study was initially intended to include accelerated corrosion testing of a series of interesting alternative coatings. However, it is well known [2] [3] [4] [5] that accelerated corrosion testing can be misleading and often show low correlation with atmospheric corrosion in real applications. Therefore, it was decided to complement the accelerated testing with natural weathering exposures at Bohus-Malmön. The natural exposure is now ongoing, and the progress will be followed and reported once a year within the MRC Corrosion Protection. In addition to the natural exposure, reference objects with some of the alternative coating systems have been inspected. Inspected reference objects include. Six bridges in Norway coated with Zinga. US Army causeway systems, a submerged steel ramp and the Statue of Liberty that has been coated with Fontezinc HR. The crowning crucifix of Uppsala dome church that has been coated with carbozinc 11 and a railway bridge in Varberg that has been coated with Eon Coat. The results from the reference object inspections are available in a separate report. [6]

2 Description of tested coating formulations

2.1.1 Bridge system (Reference)

In this study, one reference bridge system in accordance with the requirements in AMA-anläggning have been tested and evaluated along with the alternative systems. The reference system tested is composed of a zinc rich epoxy primer (90% Zn), a MIO-pigmented epoxy midcoat and a polyurethane topcoat.

2.1.2 Alternative bridge system (Hempel)

Zinc rich epoxy primers are well-established products on the market. Even so, efforts to develop new formulations with improved protection are still made. Hempel has developed a new technology, called the Avantguard series that they claim increase the amount of active zinc in the coating. The products contain an activator that ensures that more of the zinc in the coating is active. In addition to the activator, hollow glass spheres have been added to modify the physical properties of the cured coating [20]. The Hempel Avantguard was awarded with the NACE Materials Performance (MP) Corrosion Innovation awards in 2014. The product is not compliant with the current requirements in AMA-anläggning because the zinc content is less than 90% by weight.

2.1.3 Alternative bridge system (Carboline)

An alternative bridge system that fulfils the requirements for C5 according to ISO 12944-5. This system is based on a zinc rich epoxy primer that is also sold as a stand-alone coating system. The tested coating system is not compliant with the Swedish requirements in AMA-anläggning because the zinc primer is less than 90% by weight. However the primer contains electrically conducting pigment(s)/ resin.

2.1.4 Zinc Rich Epoxy (Carboline)

Carboline is one of few companies that specify a single layer zinc rich epoxy as a stand-alone system. The system is mainly specified for areas where there is no or little requirements on the aesthetics of the asset. A 100 µm single layer zinc rich epoxy coating could offer lower VOC and faster maintenance. This system was also included to be able to compare how a stand-alone zinc rich epoxy performs compared to a complete C5 system according to ISO 12944.

2.1.5 Zinga (Zinga Metal)

Zinga is a zinc-rich coating with high zinc content, 97% by weight in the dry film. According to the manufacturer, the zinc pigment in the product is produced by an atomization process, which provides high purity and tailored morphology of the zinc particles. Zinga is a physically drying coating with unlimited pot life and very short drying times, 1-4h depending on the ventilation and temperature. Application is possible in a wide temperature range, -10 °C to 45 °C. It is also relatively insensitive to moisture during curing, it is possible to apply in relative humidity of up to 90 %. The product is relatively high in VOC but with a specified nominal dry film thickness of 120-180 µm the total amount of VOC per square meter can be lower than traditional C5 systems with specified nominal dry film thickness of 320 µm. One advantage of Zinga is that the degradation of the coating in moderately corrosive atmospheres appears to progress from the outside and in, rather than via flaking and undercutting. Maintaining an aged Zinga coating can according to the manufacturer be done simply by a high-pressure wash followed by application of a new coating layer. The new layer will then (in part) dissolve the old paint and reload the coating with new zinc. This results in a coating that can be comparatively easy to maintain, especially on assets such as ships, oil platforms and in industry where a frequent ad hoc maintenance procedure can be utilized.

2.1.6 ZingAlu (Zinga Metal)

ZingAlu is a newly developed product which is very similar to Zinga. It is produced by Zinga Metal but in contrast to Zinga, the ZingAlu is pigmented with both zinc and aluminium. Since the ZingAlu is a new product, not so much is known about the possible benefits from this system.

2.1.7 Zinc Ethyl Silicate (Carboline)

Alkyl zinc silicates were developed in the 70-80´. This type of paint is cured by transesterification of alkoxy silicates. The silyl alkoxides reacts with moisture from the atmosphere to form polymeric zinc silicate. In the process, alcohol is liberated, and the final paint film is in theory completely inorganic [7]. This type of coating has previously been used extensively in the Offshore and shipping industry. Combined with a chlorinated rubber topcoat it has also been used as part of a bridge system in the Swedish infrastructure. A few reasons that it no longer is used for bridges is that the chlorinated rubber has high VOC content, and that the curing requires high humidity, which means that the application is a little more tricky compared with zinc rich epoxy primers. Some research reports [8] claim that both ethyl zinc silicate, and zinc rich coatings generally shows better corrosion protection when used as a stand-alone system, i.e. without any topcoat. It is therefore interesting to evaluate zinc ethyl silicates as a single coat system. This could provide a cost-effective coating for assets or surfaces that has no esthetical requirements. Using Zinc ethyl silicate as a stand-alone system would eliminate the troubles of a too early overcoat. The use of ethyl zinc silicate as a stand-alone system could also reduce the amount of VOC and limit the use of sensitizing chemicals such as epoxy or isocyanates.

2.1.8 Waterborne High Ratio Zinc Silicate (Tikkurila)

The first inorganic zinc silicates were discovered in the 1940's in Australia by Nightingall. The Nightingall silicates were heat cured and required baking in temperatures of about 120-230 °C, [7]. During the mid-1960´s through to the late 1970`s NASA published a series of patents related to the development of waterborne silicates that cures quickly at ambient temperatures, [9] [10] [11] [12]. The NASA patents describes various inorganic zinc silicates based on water soluble potassium silicate. The Nasa patents [12] describe a zinc silicate coating with an unusually high molar ratio of; K_2:SiO_2 = 5.3:1. During the late 1970`s the production of a silicate coating formulated according to the NASA patents was licensed to Polyset and was sold by Inorganic Coatings under the trade name IC531. Inorganic Coatings has now been deconstructed and Tikkurila OY owns an exclusive agreement with Polyset to sell the original IC531 formulation in Europe under the new trade name Fontezinc HR. The Fontezinc HR is a very interesting alternative coating for the following reasons: The coating is completely free from VOC. It contains no sensitizing chemicals such as epoxy or isocyanates. It is made without petroleum based raw materials. It is has antifouling properties and gives excellent corrosion protection. A drawback of the coating is that it is waterborne, and as such, it requires more careful pretreatment, all surfaces must be completely free from oil and dirt for the coating to be able to wet the substrate.

2.1.9 Acid Cured Waterborne Silicate (Eon Coat)

EonCoat is a NASA spinoff product from a development project aimed to produce a fast-curing concrete that would enable rapid containment of the fuel in the event of a meltdown in a nuclear reactor. The product consists of wollastonite which is a naturally occurring silicate mineral [33]. The product also contains magnesium hydroxide and phosphoric acid and would thus be categorized as an acid cured silicate coating. As the product is a ceramic, it has somewhat different properties than organic coatings; a significant difference is that it is relatively brittle. Another difference is that it does not contain any zinc and cannot offer any cathodic protection to the steel substrate. The product is interesting from an environmental standpoint because it contains no organic solvents or sensitizing hardeners [32]. It is also interesting as a maintenance system because it is a fast curing single coat system. As such it could reduce downtime when maintaining industrial or infrastructural assets. The product has shown very good corrosion resistance in accelerated tests and field tests conducted by NASA. [34] Eon Coat has been awarded the NACE Corrosion Innovation Award 2015.

3 Evaluation of corrosion protection

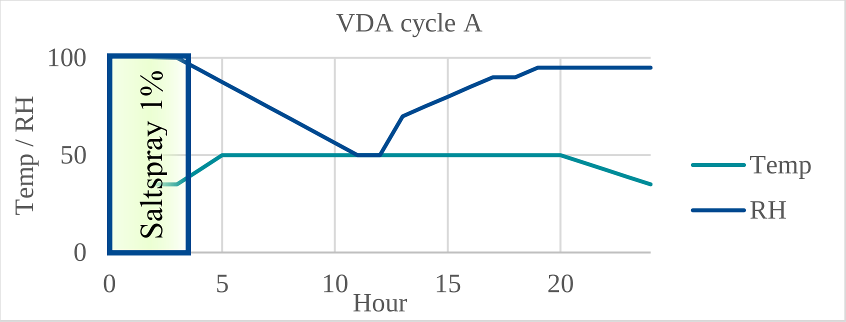
3.1 Accelerated Corrosion Testing

There is a vast array of different tests available for corrosion testing and it can sometimes be hard to choose a test that is relevant for the conditions that the coating will be subjected to during its service life. In this study we have chosen to use two different accelerated tests, both the Norsok test, ISO 12944-9 and the VDA-233-102. The ISO 12944-9 test is normally used to qualify coating systems for extremely corrosive environments such as Cx in the offshore industry. The VDA test has been developed by DIN and the German automotive industry to simulate the corrosivity in road environments. The conditions during the two tests are presented under 1.2.1 and 1.2.2 respectively.

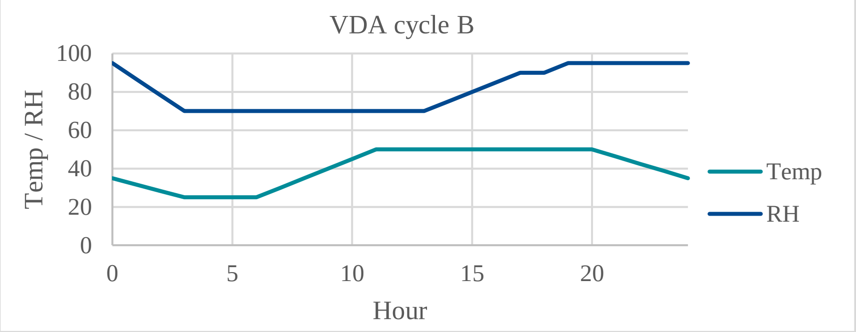
Significant differences between the tests are that the VDA use a comparatively short brine spray period. The salt used is 1 % NaCl. Whereas in the ISO 12944-9 test the samples are exposed to neutral salt spray with 5 % NaCl for about 40 % of the test duration. In the ISO 12944-9 test, the samples are rinsed from salt once during each cycle and the samples are exposed to dry periods during the UV part of the exposure. During the dry UV periods a relative humidity of about 20 % was measured inside the UV-chamber. Since there is no rinsing of samples in the VDA, the mean temperature of the samples during exposure to high salt load is higher in the VDA test

3.1.1 VDA-233-102

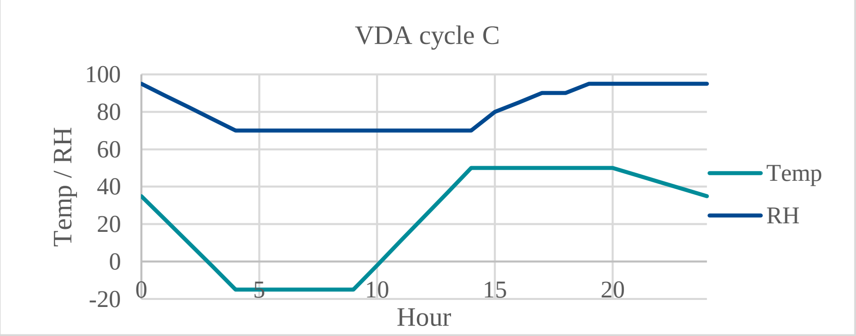
The test was performed in a ControlArt Test Chamber Type 2. The VDA 233-102 consists of three different 24 h cycles that is repeated in a specific order. The different cycles are described below. A complete test cycle (one week) consists of seven of the 24 h cycles in the following order: B, A, C, A, B, B, A. During cycle A a 1,0 % NaCl-solution is sprayed on the specimens for a period of 3 h and with a quantity of 3,0 ± 1,0 ml / 80 cm^2, h.



VDA 233-102 Cycle A



VDA 233-102 Cycle B



VDA 233-102 Cycle C

Figure 1. Control Art cabinet used for the VDA test

3.1.2 ISO 12944-9

The test was performed in three separate test chambers: a Weiss SC 1000 salt spray cabinet, a QSUN QUV cabinet and a Weiss Technic atmospheric cabinet. The ISO 12944-9 test consists of neutral salt spray for three days followed by rinsing with deionized water, and a thermal shock where the samples are cooled to -20 °C for 24 hours. The last part of the exposure is a UV/ condense exposure with cycling between humid air and irradiation with UVA light.

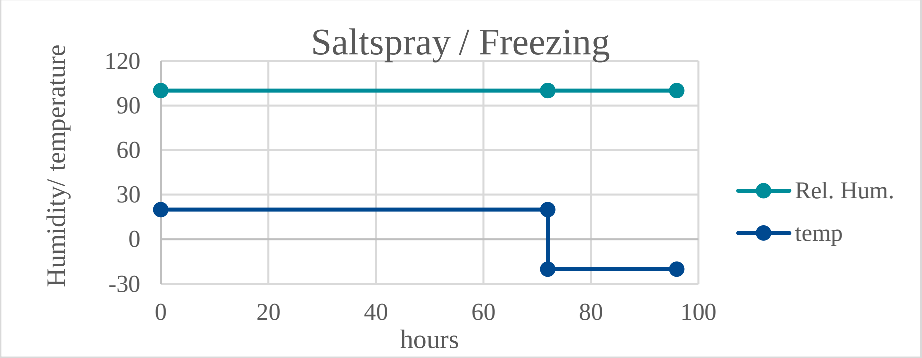


Figure 2. Temperature and relative humidity during saltspray and freezing

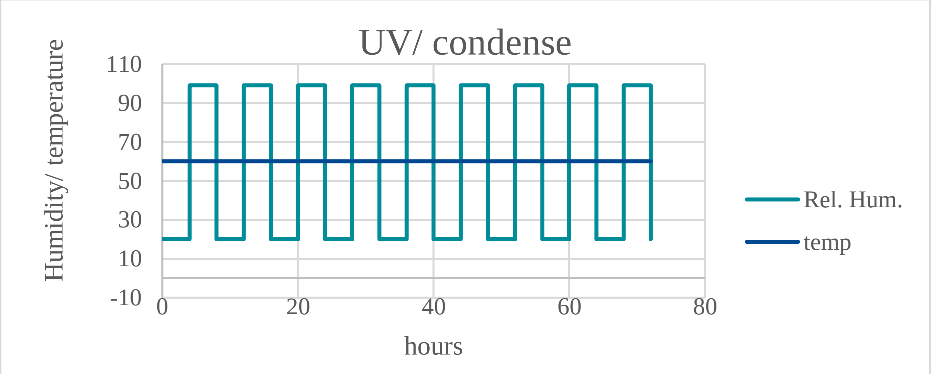


Figure 3. Temperature and relative humidity during UV and condense

Figure 4. For the ISO 12944-9 protocol, three different cabinets were used, to the right: saltspray chamber, middle: atmospheric cabinet, right: UVA and condense cabinet.

3.2 Results from accelerated tests

3.2.1 Sample preparation

All samples that have been tested in this study were supplied from the respective paint manufacturer. No application control has been performed by RISE KIMAB for any of the coatings. The specified sample preparation from RISE KIMAB was according to the following: substrate shall be hot rolled low alloyed steel. The sample specimens shall be degreased and blasted with grit abrasives to a surface cleanliness of Sa 2½ according to SS-EN ISO 8501-1. After the surface preparation, the coating system preferred by the paint manufacturer should be applied to the substrates. See list of coating systems tested in Summary of tested coating systems

Table 1. And results after assessment in Summary of corrosion assessment

Table 2.

3.2.2 Deviations from the standards

During this test, a few deviations from the standards were made:

- The VDA test requires a diagonal, manually made 1 mm wide scribe, the ISO 12944-9 requires a horizontal 2 mm wide machine-made scribe and the type testing according to AMA-anläggning (the natural exposure) requires a horizontal 1 mm wide manually made scribe. To be able to compare the results from the different exposures, it was decided to use a horizontal 2 mm wide manually made scribe for all the samples, regardless of exposure protocol.

- Many of the systems tested are single layer coating systems, as such they do not comply with the specified coating system in the Norsok standard and could never be approved according to the Norsok prequalification requirements.

- The VDA test is normally run in multiples of six weeks, usually 6 or 12 weeks are specified. The test is most often used for automotive coating systems with comparably low dry film thickness. Since industrial and infrastructural assets often have design life that far exceeds that of a car, it was decided to run all the alternative coatings in the VDA test with a duration of 24 weeks.

- The condensation/ UVA exposure included in the ISO 12944-9 protocol was performed in a QUV cabinet from Q-SUN. The OEM sample holders used for the QUV cabinet had a design that could not expose the full area of the tested sample plates. Because the coating systems made up of a single layer zinc rich coating are electrically conducting, they have in addition to the UV/ condensation been subjected to crevice corrosion at the areas covered by the sample holders. Furthermore, the edge protection of the samples had been made differently depending on where the samples were made. This resulted in that different samples had different crevice widths. In particular the Zinga, ZingAlu and Fontezinc HR samples were edge protected with a comparatively thin edge, resulting in a more narrow crevice compared to other samples. Because of this deviation the sample assessment has been limited to the area that was not affected by crevice corrosion. For the ZingAlu samples the crevice corrosion was so pronounced that it was not possible to evaluate the samples.

3.2.3 Summary of tested coating systems

Table 1. Summary of coating systems with specified coating thickness. Mean values of the measured total coating thickness and scribe depth for each coating system is indicated in the last two columns.

Make	**Description**	**Product Name**			**Specified NDFT [µm]**				**Measured [µm]**	
		First coat	Second coat	Third coat	First coat	Second coat	Third coat	tot NDFT	DFT	Scribe depth
Hempel	Alternative bridge system	Avantguard 860	Hempaprime Multi 500 Winter	Hempathane Speed-Dry Topcoat 250	40	170	50	260	294	419
Carboline	Alternative bridge system	Carbozinc 858	Carboguard 633	Carbothane 156 SG	75	130	75	280	238	320
Carboline	Zinc rich epoxy	Carbozinc 858	n/a	n/a	100	n/a	n/a	100	93	172
Carboline	Zinc ethyl silicate	Carbozinc 11	n/a	n/a	100	n/a	n/a	100	80	165
Tikkurila	Water borne inorganic zinc silicate	Fontezinc HR	n/a	n/a	100	n/a	n/a	100	75	148
Reference	Bridge system Acc AMA	EP(Zn) 90 %	EP (MIO)	PUR	40	2x100	2x40	320	316	416
Eon Coat	Waterborne acid cured inorganic silicate	EonCoat	n/a	n/a	500	100	n/a	600	571	652
Zinga Metall	One component zinc rich	Zinga	n/a	n/a	120	n/a	n/a	120	108	172
Zinga Metall	One komp component zinc rich	Zinga	n/a	n/a	180	n/a	n/a	180	159	221
Zinga Metall	One komp component zinc/aluminum	ZingAlu	n/a	n/a	120	n/a	n/a	120	120	183

3.2.4 Summary of corrosion assessment

Table 2. Summary of results from assessment after accelerated corrosion testing according to ISO 12944-9 and VDA (24 weeks)

Assesment Method	**Requirement after testing**	**Zinga 120**	**Zinga 180**	**Carboline EtZnSi**	**Carboline Ep (Zn)**	**Carboline** (Alternative bridge sys.)	**Hempel** (Alternative. Bridge sys.)	**Reference** (AMA bridge sys.)	**Tikkurila HRZS**	**ZingAlu 120**	**Eon-coat**
ISO12944-9 (NORSOK) 25 weeks											
Pull-off test ISO 4628*	5 Mpa	7,7 (6,0)	7,9 (4,3)	5,5 (7,9)	5,2 (7,8)	8,2 (7,3)	7,5 (7,3)	11,2 (12,8)	8,8 (5,8)	n/a (2,3)	n/a (3,6)
Crrosion at scribe **	3,0 mm	1,9	1,6	3,6	0,7	3,8	5,5	3,5	0,3	n/a	n/a
Rust grade ISO 4628***	0	0, 1, 1	0, 0, 1	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 1, 1	5, 5, 5	5, 5, 5
Blistering ISO 4628***	0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	n/a	n/a
VDA 233-102 (new) 24 weeks											
Pull-off test ISO 4628*	n/a	0,9 (6,1)	0,9 (4,3)	5,1 (7,9)	4,5 (7,8)	6,7 (7,3)	6,3 (7,3)	7,5 (12,8)	5,9 (5,8)	0,0 (2,3)	0,6 (3,6)
Crrosion at scribe **	n/a	n/a	n/a	1,2	0,6	2,6	3,5	2,7	0,6	>10	>20
Rust grade ISO 4628***	n/a	5, 5, 5	5, 5, 5	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	3, 3, 4	0, 0, 0
Blistering ISO 4628***	n/a	0, 0, 0	0, 0, 0	0, 0, 0,	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	3(S5), 3(S4), 2(S4)

Note: * number in brackets is the adhesion value on the nonexposed reference panel, ** numerical mean value for all three panels, *** values for each exposed panel is reported separately

3.3 Electrochemical measurements

Measuring the Open Circuit Potential, (OCP) is a method of getting a first idea of the reactivity of a galvanically active coating system. When a sample is immersed into a solution, a double layer of electrons and ions is formed at the interface between the sample and the solution. Ions are attracted to the surface and balanced by electrons in the metal with equal charge but opposite polarity. This double layer gives rise to a potential described by Nernst's equation:

$$E = E^0 - \frac{RT}{zF}\ln Q$$

Where E is the potential, E^0 is the standard potential of the material, R is the general gas constant, T is the temperature, z is the number of electrons transmitted in the reaction, F is Faraday's constant and Q is the reaction rate. The relationship between Q and E gives information on the driving force for the dissolution of the metal.

$M \rightarrow M^{z+} + ze^-$

Simply described, noble metals have more positive potentials and metals such as aluminum and zinc have more negative potentials. In a galvanic system the metal with lower potential will corrode first. OCP often varies with time in solution and a shifting OCP is an early indicator that surface properties are changing. Changes in OCP can occur as a result of corrosion, degradation of a protective layer, water ingress into a coating or depletion of zinc in a zinc pigmented coating. In the case of a zinc rich coating on a scribed steel surface, the measured potential will be a mixed potential between that of pure zinc, (approx. -1,0 V) and that of pure steel, (approx. -0,6 V) versus a Ag/ AgCl reference electrode. If the measured potential is close to -1,0 V that is an indication of corrosion of zinc, whereas a potential close to -0,6 V is an indication of corrosion on steel. If the potential is somewhere between -1,0 and -0,6 that indicates that both steel and zinc is corroding. The OCP can therefore be used as a tool to measure if the zinc coatings are able to give a galvanic protection to the steel. Generally, a rule of thumb is that a mixed potential lower than -0,8 V indicates a steel/ coating system where the steel is galvanically protected. To investigate the galvanic activity of the tested coatings all coatings have been investigated by measuring the OCP variation over time.

3.3.1 Results from electrochemical measurements

All zinc coatings without top-coat have been investigated by measuring the OCP variation over time, see Figure 5. From the measurements it is clear that different coatings have different galvanic activity, Zinga and ZingAlu was the most active ($E < -1,0$ V), Zinc ethyl silicate is less active than Zinga ($E \sim 0,95$ V) but more active than zinc epoxy ($E \sim 0,88$ V), Fontezinc HR showed initial passive potentials ($E \sim -0,3$ to $-0,5$ V). First after about 20 hours the potential indicates galvanic protection ($E \sim -0,80$ V). All coatings except ZingAlu provided galvanic protection to the steel for more than 400 hours.

To further investigate the galvanic action of the zinc systems, OCP measurements on scribed samples were performed, see Figure 6. The figure show that most stand-alone zinc rich coatings can provide a galvanic protection to the scribe. ZingAlu appears to be relatively quickly depleted as the corrosion potential rises comparatively fast. Fontezinc HR again showed slow initiation of the galvanic action and was able to protect the steel for a comparatively short period indicating a poor galvanic protection.

The three coat systems could only be studied on samples with a scribe, see Figure 7. The AMA reference system and Hempels system were very similar. Both were able to protect the scribe galvanically for about ten hours. In comparison, the Carboline alternative system was able to protect the scribe galvanically for about 75 hours. However, it is expected that the galvanic action depends on the thickness of the zinc primer. The nominal film thickness of the Carboline system was almost twice as thick as the other systems. Using the Säberg coating drill method the primer thicknesses was measured to be 75 µm for the Carboline system 55 µm for the AMA system and 45 µm for the Hempel system. Regardless of the different film thicknesses it is interesting to note that both zinc rich coatings with 80 % zinc by mass, gave at least similar galvanic protection as the 90 % zinc AMA reference system.

It is interesting to compare the galvanic properties between bare zinc coatings and topcoated zinc coatings, see Figure 8. The non-topcoated zinc rich epoxy gave galvanic protection up to about three times longer than corresponding system with the same zinc rich epoxy as primer. This result is most probably due to a much larger anodic surface area for the stand-alone zinc epoxy. In the three-coat systems, the available anodic surface area is limited to the exposed zinc epoxy in the vicinity of the scribe. And the zinc coating has a much larger area of exposed zinc. The cathode/ anode area ratio might also differ because of different modes of water uptake by the zinc coating. In the topcoated samples the water must diffuse laterally under the topcoat at the scribe. In the corresponding non-topcoated zinc water might diffuse into the coating across the film in addition to lateral diffusion at the scribe.

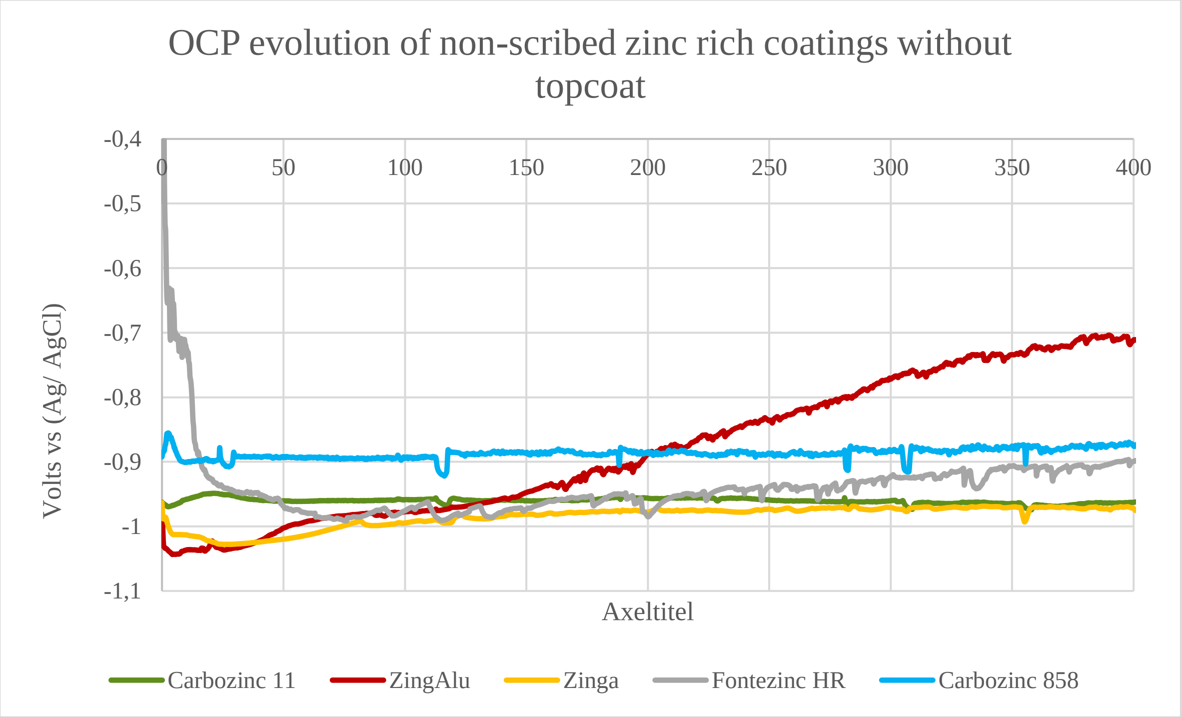


Figure 5. Open Circuit Potential measurements of non-scribed samples of zinc rich coatings without topcoat.

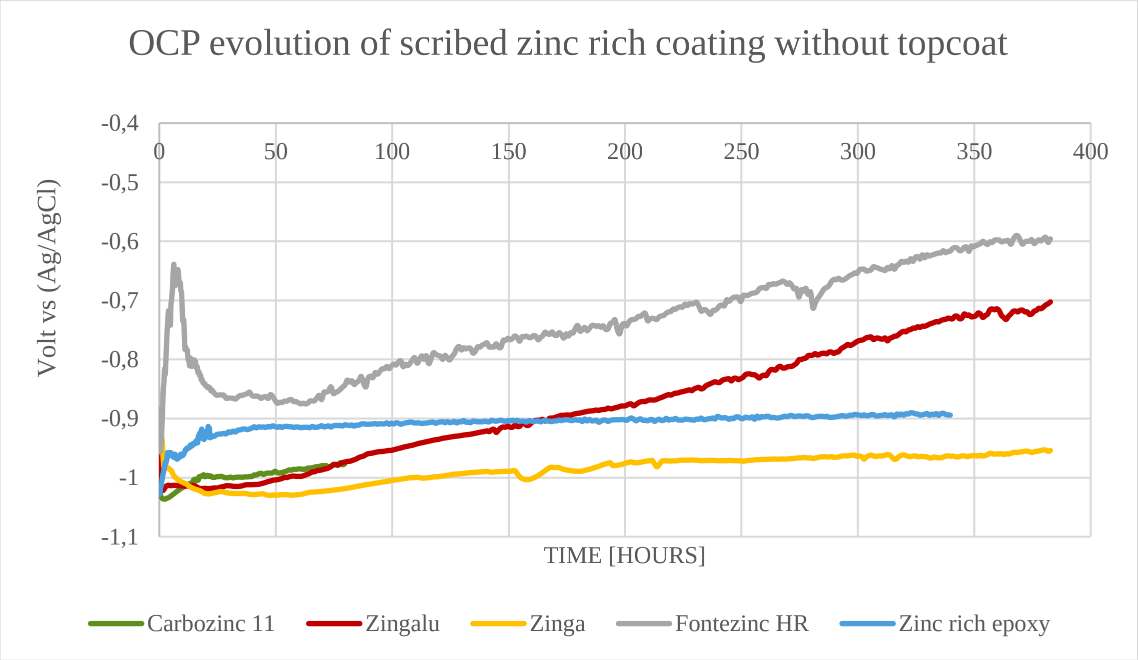


Figure 6. Open Circuit Potential measurements of scribed samples of zinc rich coatings without topcoat. The continuous OCP evolution of Carbozinc 11 was disrupted by reference electrode malfunction during the experiment. The OCP for Carbozinc 11 at the end of the experiment was -0,99 V.

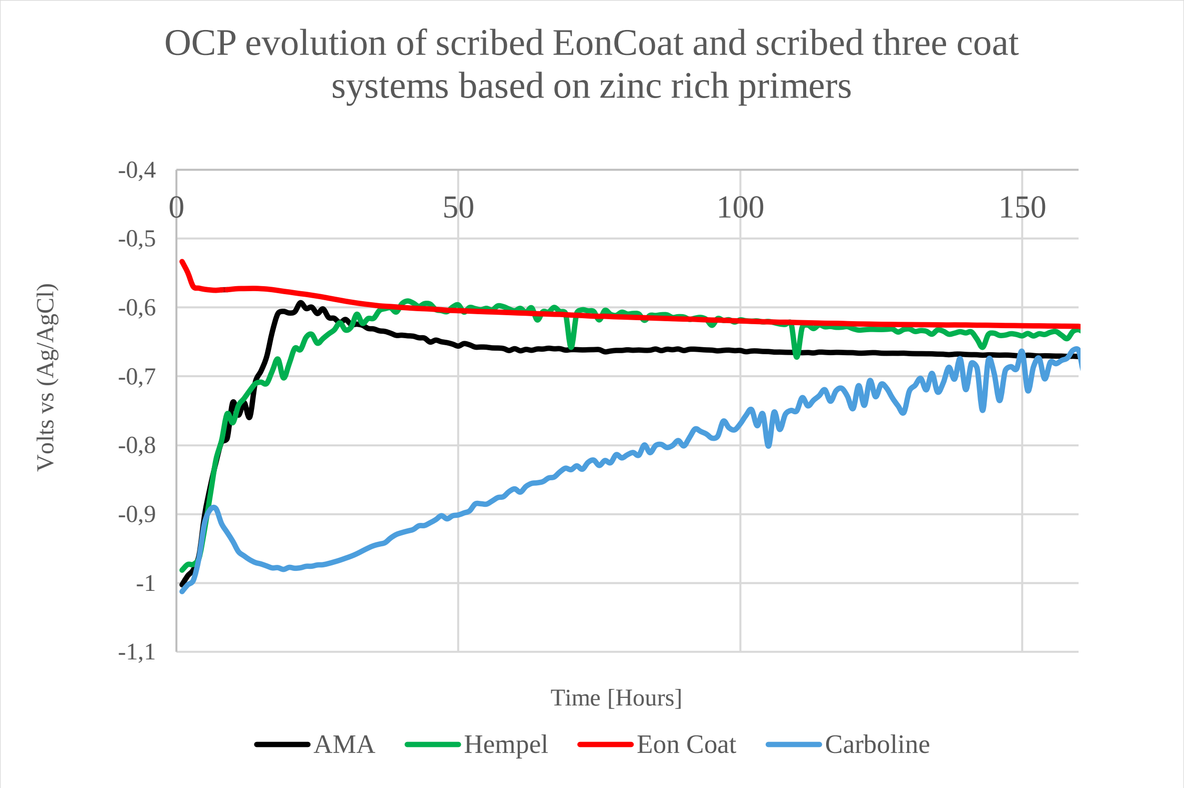


Figure 7. Open Circuit Potential evolution of alternative three coat bridge systems and Eon Coat compared with AMA approved three coat system.

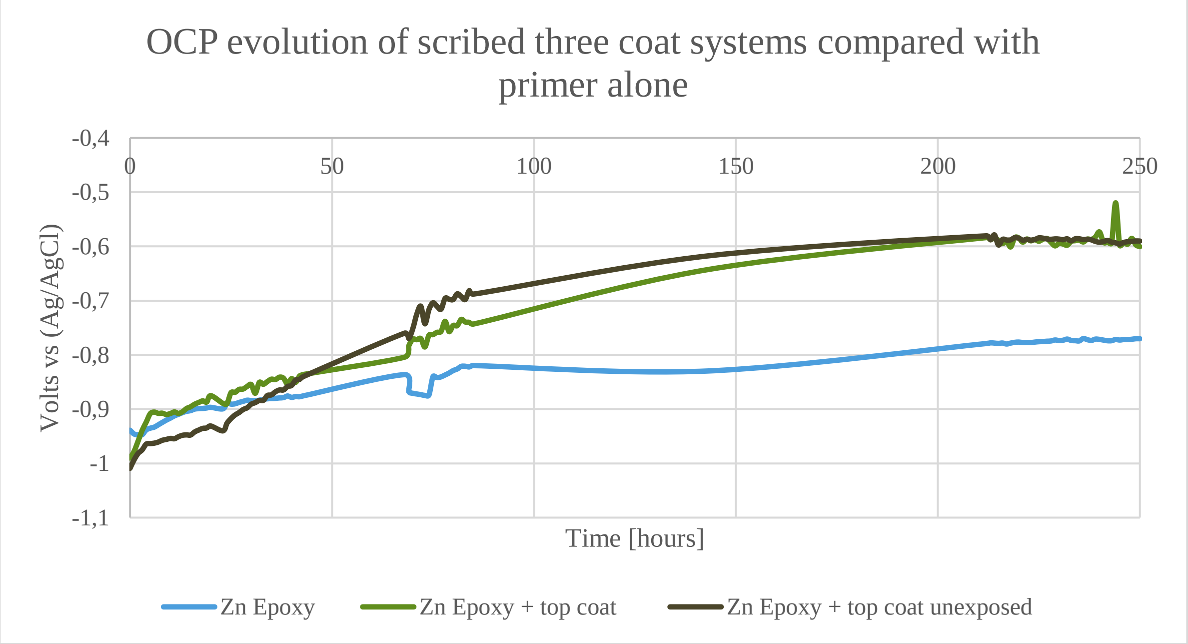


Figure 8. Open Circuit Potential measurements of scribed samples coated with Carbolines systems: Carboline three coat system pre-exposed in VDA 24 weeks, (Green). Carboline three coat system without pre-exposure, (Black). Carboline zinc epoxy primer without topcoat, (Blue).

3.4 Field exposure at Bohus-Malmön

The complementing field exposure at Bohus-Malmön was started on the 9th of October 2018. Figure 9 is a picture taken of the samples on the 26th of May 2020 after about 1,5 years. The zingAlu samples have started to rust and the Eon Coat samples have sterted to flake with adhesive failure between the topcoat and the basecoat. Other than that it is too early to draw any conclusions from the field exposure. Reoccurring ocular examination will be performed and reported yearly within MRC Corrosion Protection. Destructive evaluation of the samples will be performed when significant deterioration has been established.

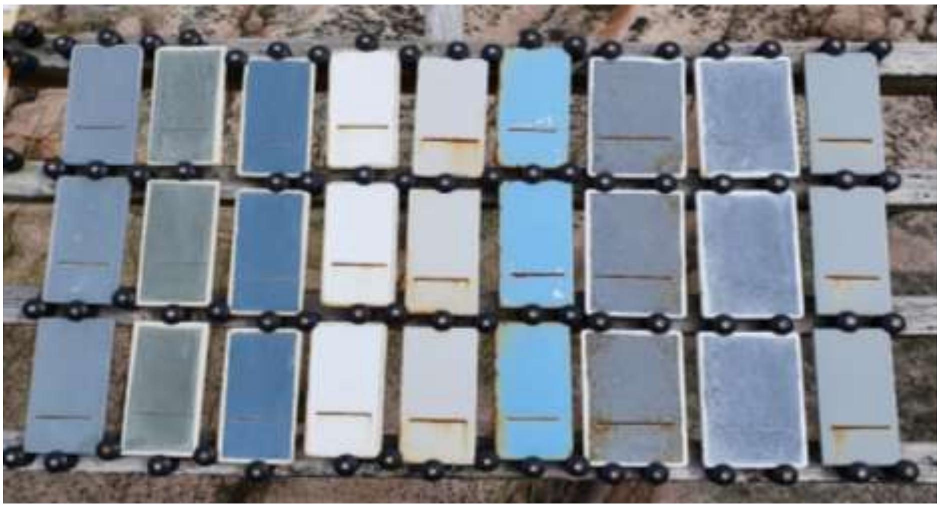


Figure 9. Picture from the start of the field exposure, from left to right: Fontezinc HR, Carboline Zinc ethyl silicate, Carboline zinc rich epoxy, Carboline alternative bridge system, Hempel alternative bridge system, Eon Coat, ZingAlu, Zinga, AMA bridge system.

4 Discussion

The Zinga systems performed much better in the ISO 12944-9 test compared with the VDA test. The VDA protocol has an overall longer wet time and a higher mean temperature (above 40 °C) during exposure to chlorides. The ISO 12944-9 test includes periods of dry air during the UV part of the condense/ UV cycle. As a result of this, much more insoluble zinc corrosion products can be seen on the samples exposed in the ISO 12944-9 test. It is well known that metallic zinc coatings require periods of dry conditions to perform at their best. Consequently, salt spray or similar tests with high humidity often gives poor correlation to outdoor atmospheric corrosion tests on zinc rich coatings. The combined effect of lower temperature and longer dry periods is probably one reason why the Zinga systems performed better in the ISO 12944-9 test, it could therefore well be that Zinga will also perform much better in the field exposure at Bohus-Malmön.

By contrast, the three-coat epoxy systems performed comparatively worse in the ISO12944-9 test. Perhaps the thermal shock included in the ISO 12944-9 could induce cracking and contribute to delamination around the scribe? This hypothesis is supported by comparatively large dissimilarities in thermal expansion coefficient between substrate and coating for the three-coat systems. For the Eon-coat samples the thermal shock was even more detrimental and resulted in de-adhesion from the substrate, leaving the steel completely unprotected. For the Eon-Coat samples delamination effect was probably pronounced by a relatively brittle coating.

The zinc pigmentation in zinc rich coatings behave differently depending on the coating vehicle. In other words, the properties of the binder and/ or other additives can affect the electrochemical activity of the zinc pigment. Silicate binders can inhibit the anodic reaction on zinc which makes the coating less reactive. Depending on the ratio of zinc and binder, epoxy binders can insulate the zinc pigmentation and thereby limit the galvanic effect from the zinc pigmentation. The Avantguard zinc is formulated with a proprietary activator that increase the activity of the zinc. Carbozinc 858 has additives (other than zinc) that increase the electrical conductivity of the coating. The OCP measurements performed in this study indicates that the formulations with highest galvanic activity was Zinga and ZingAlu. The least active zinc was found in Fontezinc HR. The pigmentation in Carbozinc 858 and Carbozinc 11 were found to be intermediate. This order of activity could explain some of the results from the accelerated tests. Zinga and ZingAlu are pigmented well above CPVC with a very active zinc, consequently the coating gives a good cathodic protection. On the other hand, the pigmentation is relatively quickly depleted. A faster consumption of zinc is probably why the Zinga formulations did not perform well in the VDA test. The corrosion of the zinc pigmentation in Fontezinc HR is inhibited by the silicate binder, as a result the zinc particles are not consumed as fast and the coating gives a comparatively poor galvanic protection. But the coating is not depleted as fast. Interestingly, in this study, the stand-alone zinc rich coatings with the lowest galvanic action gave the better results in the accelerated tests.

There are several mechanisms by which zinc rich coatings can protect steel, these include:

- Galvanic protection
- Barrier protection
- Inhibition of the steel
- Buffer the pH at the steel/ coating interface

It is clear that the expression of these mechanisms can be tailored by choosing an appropriate binder, additives and degree of pigmentation. Depending on the exposure it is not always best to have an active zinc. Rather, the key to success appears to be a moderately active zinc pigmentation, see graphical presentation in Figure 10. The zinc activity can be controlled by:

- Inhibition of the zinc
- Activation of the zinc
- Electrically conductive additives
- Amount of pigmentation
- pH at the coating/ substrate interface

OCP	Increasing galvanic activity	VDA	Increasing corrosion at scribe	Norsok	Increasing corrosion at scribe
Zinga	↑	Zinga	↑	Zinc ethyl silicate	↑
Zinc ethyl silicate		Zinc ethyl silicate		Zinga	
Zinc rich epoxy		Zinc rich epoxy		Zinc rich epoxy	
Water borne zinc silicate		Water borne zinc silicate		Water borne zinc silicate	

Figure 10. Trends in galvanic activity as measured by OCP, compared with trends in corrosion at scribe after accelerated corrosion testing.

5 Conclusions

- The systems with best result after testing according to the exposure protocol in ISO 12944-9 was a single layer of zinc rich epoxy, Carbozinc 858.

- The system with best result after testing according to the VDA exposure protocol for 24 weeks was Carbozinc 858 and Fontezinc HR.

- Single coat systems composed of zinc ethyl silicate, waterborne zinc silicate and zinc epoxy all performed better than the three-coat systems.

- The three bridge systems gave similar results in both accelerated tests. The ISO 12944-9 protocol gave slightly higher rust creep from scribe suggesting that the ISO protocol was somewhat more challenging to the bridge systems.

- Eon Coat appear to be sensitive towards thermal shock.

- Zinga performed well in the ISO12944-9. On the other hand, Zinga gave very poor results in the VDA test. In that respect, the Zinga formulation gives a very active galvanic protection that behaves much like hot dip galvanizing.

- Higher zinc content does not necessarily give a better cathodic protection.
- The longevity of the cathodic protection does not necessarily reflect the longevity of the coating.
- When formulating zinc rich coatings, it can be vital to fine tune the activity of the zinc pigmentation to optimize the galvanic protection for the intended use.

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