Modified ASTM D610 Analysis of Zinc-Nickel Nanolaminate for Bolt Corrosion Mitigation

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ABSTRACT

This paper will present both laboratory and field trial results as evaluated using a modified form of ASTM D610[VII] for corrosion evaluation of fasteners and compares consistency and accuracy of this approach for both lab and field measurement of degree of corrosion. The modified ASTM D610 methodology is used to evaluate a novel, nanolaminated zinc-nickel alloy system. The majority of steel fastener systems are protected from corrosion using one or more of hot dip galvanizing, electrogalvanizing, poly-tetra fluoroethylene (PTFE), and cadmium. Nanolaminated zinc-nickel has improved corrosion performance as compared to these conventional systems. This paper presents combination of laboratory and field trial information that compares the performance of the nanolaminated zinc nickel system in multiple laboratory and field conditions with incumbent coating technologies.

Key words: Nanolaminate, Nano-structure, metallic coating, multilayer coating, Zinc-nickel, zinc-nickel, deposit, composite, corrosion protection, fastener, bolt, electrodeposition, hot dip galvanize, cadmium, PTFE

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INTRODUCTION

ASTM D610[(VII)] is an industry consensus standard that was originally published in 1985 and most recently renewed in 2012. This standard describes a procedure for the evaluation of corroded, two-dimensional surface. The objective of this standard is to reduce the variability due to subjectivity in evaluating the degree and type of corrosion observed on the surface. ASTM D610 provides both visual guides and an index for the assignment of the degree of corrosion and is especially useful in providing a consistent metric for corrosion assessment in field conditions. It is especially useful in the comparative analysis of different coating systems in various test and field environments. ASTM D610 is widely used for evaluating the degree of corrosion on simple, surface geometry, however the usefulness of this method for evaluation of complex geometry has not been evaluated. The purpose of this paper is to evaluate an adaptation of ASTM D610 for evaluation of corrosion on the complex geometry of bolting systems. The authors provide examples of the ASTM D610 application for comparison of the performance of standard galvanize, cadmium, PTFE coatings with a novel nanolaminated coating system.

"Nanolaminated coatings" refer to a class of materials that are comprised of nanometer-scale particles deposited in layers that vary in composition, phase, material microstructure[1] or a combination of these. Nanolaminated metallic coatings provide a thin, corrosion resistant layer that protects the metallic substrate from the environment. Through an electrochemically controlled deposition process, precisely defined configurations of layered metal alloys are assembled onto the substrate. The deposition process can be controlled to produce nano-scale layers with unique interfacial properties resulting in enhanced corrosion resistance, elastic modulus, strength, hardness, adhesion, and fracture toughness in combinations uniquely different from conventional material processing.[i,ii] The dramatic improvements in properties and performance, as compared to conventional metal alloys, are a result of the atomic structure of the interfaces between the nano-layers. Evaluation of nanolaminate plastic deformation using atomic simulations, dislocation theory and crystal plasticity modeling describes the laminate deformation mechanisms that result in the improvements in properties and performance.[3iii]

A recent paper described the application and laboratory testing of the nanolaminated zinc-nickel alloy coatings applied to threaded studs and nuts.[iv] These lab results indicate significant enhancement of corrosion resistance as compared to conventional coatings. In addition, the United States Coast Guard has carried out an independent analysis and field trial of the nanolaminated zinc-based coating system for bolts over the period of two years.[v] Findings of this field trial confirmed zinc nanolaminate superior performance as compared to current industry solutions.

In the offshore oil & gas industry, bolts continue to provide corrosion challenges (Figure 1). Considering that facility design life can be 25 years or more, service conditions range from sub-zero to 400 °C, and thickness of any coating is limited by the thread tolerances, the mitigation of bolt corrosion is challenging. Nanolaminated coatings of 5-15 microns offer a protective barrier that is within the thickness constraints of thread tolerances. Recent advances in manufacturing processes have made nanolaminated zinc-nickel coatings cost comparative to their traditional counterparts.[vi] This paper presents the interim results of a comparative offshore bolt field trial and recently completed laboratory evaluation of bolts with the same coating systems used in the field trial. After 30 months of field

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[1] Microstructure is intended to refer to a material's microstructural or nanostructural characteristics, including density, grain size, grain geometry, crystal structure (i.e. BCC, FCC, HPC, etc.) and crystal orientation (or lack thereof as in amorphous metals).

exposure the nanolaminated Zinc-nickel coated bolts are performing measurably better than its peers (as evaluated with ASTM D610[vii]). This outcome aligns with the accelerated laboratory test results.

Figure 1: Example of Bolt Corrosion

MATERIALS and METHODS

NanoGalv® (Nanolaminated Zinc-Nickel Alloy) Coatings

Nanolaminated Zinc-Nickel (Zinc-nickel) Alloy coatings is a proprietary product, produced in an electrochemical process that involves immersing parts that are to be coated into a formulated electrolyte containing zinc and nickel metal ions as well as other electrochemically-active additives and applying a modulated electric field across a cathode (the substrate itself) and an anode. Application of this process[viii] results in the deposition of micron-thick coatings in nanometer thick sub-layers of alternating Zinc-nickel compositions through the coating thickness.

For fasteners referenced in this paper, the nanolaminated coating was applied to 5/8”x3.25” ASTM A193 B7 studs, ASTM A194 2H heavy hex nuts and ASTM F436 flat washers followed by a trivalent chromate passivate. The thicknesses of these fasteners were measured via XRF and are reported in Table 1.

Accelerated Corrosion Testing

An independent third party conducted the accelerated corrosion tests comparing the performance of nanolaminated Zinc-nickel fastener coatings versus current industry alternatives. A total of five industry alternatives were commercially obtained on 5/8” ASTM 193 B7 studs and ASTM A194 2H hex nuts and tested in parallel with the nanolaminated Zinc-nickel fasteners. These five industry alternatives are listed in Table 1 along with their measured “off the shelf” thicknesses.

Table 1. Laboratory Tested Coating Systems

Coating Types	Avg. Stud Coating Thickness, microns	Avg. Nut Coating Thickness, microns
ZnNi Nanolaminate	19.4	7.9
Hot Dip Galvanize	14.1	22.5
Electrogalvanize	7.1	3.8
PTFE	31.9	32
Cadmium	8.5	6.3
Bare Steel	N/A	N/A

Salt Spray (Fog) Performance

Salt fog performance testing was run in accordance with ASTM B117-16[(ix)] Samples were visually evaluated (1x magnification) every 24 hours, except weekends and holidays, for the presence of red rust in accordance with ASTM D1654 Procedure B and the technician's best estimate.[x] Once the first red rust was observed on a sample, it was photographed every 48 additional hours (except on weekends and holidays). Testing was stopped once samples had reached approximately 10% red rust or once 4000 hours of testing had elapsed.

Cyclic Corrosion Performance

General Motor's standard GMW[2] 14872 "Cyclic Corrosion Laboratory Test" is an accelerated laboratory-corrosion test method that is used to determine the corrosion resistance of automotive assemblies and components.[xi] It is thought to be effective for correlating accelerated corrosion test results with field corrosion degradation due to mechanisms including general, galvanic, crevice etc. This test is cyclic in nature, i.e.; test specimens are repeatedly exposed to changing test conditions over time.

Technicians inspected for the presence of red rust per ASTM D1654 every 24 hours (1 cycle) except on weekends and holidays. Using the technician's best estimate, the number of cycles to initial red rust, cycles to 5% red rust, and cycles to 10% red rust were documented along with photos of the samples after 25 and 50 cycles.

Field Trial Evaluation

In addition to laboratory testing, field trials of nanolaminated Zinc-nickel alloy coatings applied onto ASTM A193 B7 steel studs, ASTM A194 2H nuts and washers have been completed and are underway in various environments, including tropical offshore. In these field trials, the Zinc-nickel nanolaminated coatings are compared against incumbent cadmium + PTFE, and galvanized control samples.[xii] In one field trial, being carried out on a rig in a marine, tropical environment (Offshore Rig Trial), the coated fastener sets are installed on twelve separate flanges at four different locations around an offshore platform. The fasteners are arranged so that a least one of each type of bolt coating is installed on each flange at various locations throughout the facility.

[2] General Motors Worldwide, 300 Renaissance Ctr., Detroit, Michigan 48226

Figure 1. Typical Field Trial Installation

Data collection and evaluation are important to obtain representative and comparable information in all field trials. In the Offshore Rig Trial, the relative bolt locations on the flange and corrosion performance of the nanolaminated Zinc-nickel and incumbent coating systems have been reported on twice yearly basis. While the observations made by the inspectors are valuable, inconsistencies assessment terminology, observations regarding degree of corrosion and scales used for evaluating results have been inconsistent between reporting periods. This reporting aspect of the field trial is where the value is generated and required a more standardized and quantitative approach.

Utilization of ASTM D610 for Laboratory and Field Trial Data Evaluation

A search of various industry standards revealed several standardized methodologies for evaluating coated samples in corrosive environments such as ASTM D610, ASTM D1654 and ASTM B537. Among these standards, ASTM D610 alone contained specific visual guidance for measuring the degree of corrosion. The current ASTM D610 standard contains visual guides for evaluating corrosion on flat surfaces as well as a numerical scale for attributing degree of corrosion to an integer number between 1 – 10. ASTM D610 does not, however, include any methodology for evaluating complex geometries, such as fasteners, without introducing a large degree of operator bias. Therefore, standardized methodology is proposed, which adapts the rankings/grades and visual cues of ASTM D610 in a format amenable to fastener geometries.

In order to facilitate observer assignment of indices to indicate degree of red rust on the individual fasteners, the visual guides contained in ASTM D610 have been modified to reflect the observable surfaces of the fastener. This guide provides both a common approach to assessing degree of red rust as well as an indication of the surfaces that should be photographed if a record of the rated components is desired. (See Figure 3)

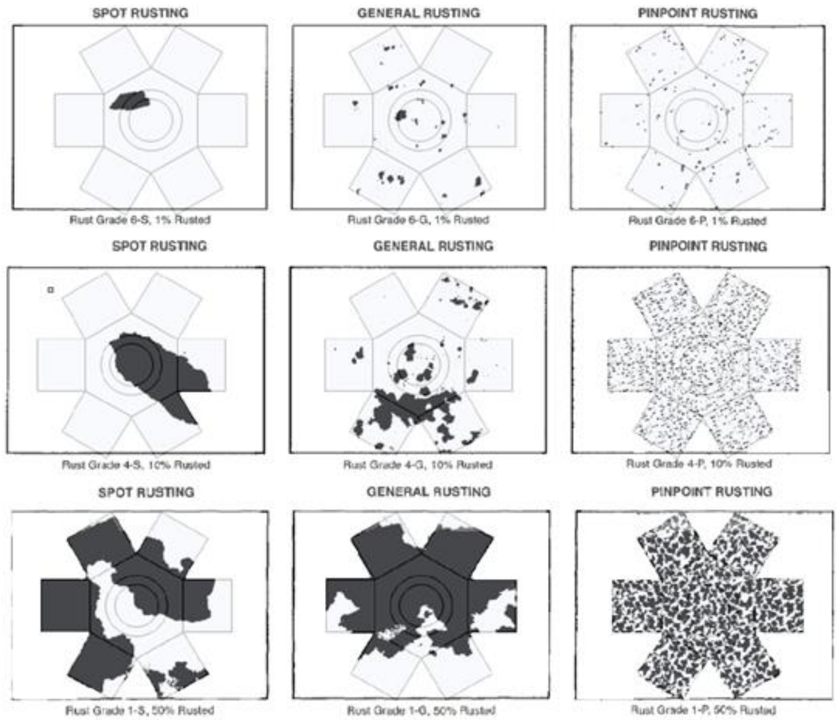

Figure 3: Visual cues provide operator's with references for red rust area percentages and corrosion type based on exposed fastener surfaces.

The visual cues (Figure 2) were adapted from Figures 1, 2 and 3 of ASTM D610 and allow inspectors to determine the type and degree of rusting present on a fastener's surface from a visual aid rather than relying on an inspector's best estimate. From these visual cues, the inspector can assign a rust grade of 0-10 based on the surface area of the fastener covered by red rust and a modified ASTM D610 scale (Table 2). This modified D610 scale collapses the rust grades of 9, 8, 7 and 6 into a single observable rust grade (6) as field inspectors cannot be expected to visually discern the difference between 0.01% and 1.0% red rust.

Table 2 : Modified ASTM D610 Rust Ratings

Original ASTM D610 Rust Grade	New Rust Grade	Percent of Surface Rusted
10	10	Less than or equal to 0.01 percent (New interpretation: no observable rust)
9	6	Greater than 0.01 and up to 0.03 percent (New interpretation: first observable rust)
8		Greater than 0.03 and up to 0.1 percent
7		Greater than 0.1 and up to 0.3 percent
6		Greater than 0.3 and up to 1.0 percent
5	5	Greater than 1.0 percent and up to 3.0 percent
4	4	Greater than 3.0 percent and up to 10.0 percent
3	3	Greater than 10.0 percent and up to 16.0 percent
2	2	Greater than 16.0 percent and up to 33.0 percent
1	1	Greater than 33.0 percent and up to 50.0 percent
0	0	Greater than 50 percent

RESULTS

The coated bolt assemblies were evaluated both in accelerated corrosion environments and in the Offshore Rig Trial environment so that comparisons could be made of the relative performance of the various coatings in the two conditions.

Salt Spray (Fog) Performance Results

Table 3 summarizes the time to 10% red rust based on the technician’s best estimate. In general, the nanolaminated Zinc-nickel far out performed the other fastener systems as samples reached the end of test (4000 hours) with no red rust.

Table 3 : Salt Fog Test Results

Coating Types	Salt Fog Hours to 10% Red Rust
Zinc-nickel Nanolaminate	4000*
Hot Dip Galvanize	677
Electrogalvanized	168
PTFE	840
Cadmium	533
Bare Steel	36

*Test terminated at 4000 hours. None of the Zinc-nickel nanolaminate samples reached 10% red rust.

Figure 4, Figure 5, and Figure 6 show the amount of red rust found on three of the selected coatings at the point when they reached 10% red rust (or in the case of the nanolaminated Zinc-nickel alloy coating, when the test was terminated). The D610 analysis results are shown above the respective Figure. In this test the nanolaminated Zinc-nickel coating evaluation was terminated at 4000 hours but there was no red rust, see Figure 5. Salt fog testing conducted by Modumetal, the Zinc-nickel nanolaminate manufacturer, has exceeded 20,000 hours without red rust appearance.

Zn-Ni Nano-laminate						
Sample ID	Stud 1. NL.	Washer 1.NL.	Washer 2.NL.	Nut 1.NL.	Nut 2.NL.	Total Rust Percentage
Rust Percentage - Component	0%	0%	0%	0%	0%	0%
ASTM D610 Rating	10	10	10	10	10	10

Figure 5: Condition of Zinc-nickel Nanolaminate Sample after 4000 hours salt fog.

PTFE						
Sample ID	Stud 1. PTFE.	Washer 1.PTFE.	Washer 2.PTFE.	Nut 1.PTFE.	Nut 2.PTFE.	Total Rust Percentage
Rust Percentage - Component	14%	N/A	N/A	10%	6%	7%
ASTM D610 Rating	3	N/A	N/A	4	4	4


Figure 6: Condition of PTFE Sample after 840 hours salt fog

Electrogalvanized						
Sample ID	Stud 1. EG.	Washer 1.EG.	Washer 2.EG.	Nut 1.EG.	Nut 2.EG.	Total Rust Percentage
Rust Percentage - Component	11%	0%	0%	0%	0%	3%
ASTM D610 Rating	3	10	10	10	10	5


Figure 7: Condition of Electrogalvanized Sample after 168 hours salt fog.

Cyclic Corrosion Performance Results

Table 4 summarizes the cyclic corrosion test GMW 14872 based on the "best estimate" visual observations made by the third party technician (not evaluated using D610).

Table 4
Summary of GMW 14872 Cyclic Corrosion Test

Coating Types	Cycles to 10% Red Rust	% Red Rust 25 Cycles	% Red Rust 50 Cycles
Zinc-nickel Nanolaminate	No red rust after 50 cycles	0	0
Hot Dip Galvanize	50	5	10
Electrogalvanized	17	100	100
PTFE	18	30	75
Cadmium #2	~50	5	7
Bare Steel	12	100	100
Cadmium #2	~50	5	7

Figure 8 and Figure 9 are the Zinc-nickel nanolaminate and hot dipped galvanized test assemblies after 50 cycles, respectively. The ASTM D610 evaluation results are shown above the photos.

Zn-Ni Nano-laminate						
Sample ID	Stud 1. NL.	Washer 1.NL.	Washer 2.NL.	Nut 1.NL.	Nut 2.NL.	**Total Rust Percentage**
Rust Percentage - Component	0%	0%	0%	0%	0%	0%
ASTM D610 Rating	10	10	10	10	10	10

Figure 8: Zinc-nickel Nanolaminate Sample after 50 Cycles

Hot Dipped Galvanized						
Sample ID	Stud 1. HDG.	Washer 1.HDG.	Washer 2.HDG.	Nut 1.HDG	Nut 2.HDG.	**Total Rust Percentage**
Rust Percentage - Component	46%	0%	0%	4%	3%	13%
ASTM D610 Rating	1	10	10	4	5	3

Figure 9: Hot Dipped Galvanized Sample after 50 Cycles

Field Trial Performance Results

The following time-lapse progressions are from flanges that are part of the above-mentioned field trial being performed in a tropical offshore environment. Figure 10 shows the time progression for Cd + PFTE with the corresponding modified ASTM D610 rating. Figure 11 is the progression for galvanized. Figure 12 and Figure 13 are similar progressions for Nanolaminated Zinc-nickel.

Cd+PTFE			
Monitor Date	14-Jul	15-Jul	16-Jan
Months in Service	12	24	30
Total Red Rust %	0%	7%	7%
ASTM D610 Rating	10	4	4

Figure 10: Field Trial Time Progression: Cd/PTFE

Hot Dipped Galvanized			
Monitor Date	14-Jul	15-Jul	16-Jan
Months in Service	12	24	30
Total Red Rust %	3%	6%	6%
ASTM D610 Rating	5	4	4

Figure 11: Field Trial Time Progression: HDG

Zn-Ni Nanolaminate 1			
Monitor Date	14-Jul	15-Jul	16-Jan
Months in Service	12	24	30
Total Red Rust %	0%	2%	2%
ASTM D610 Rating	10	5	5

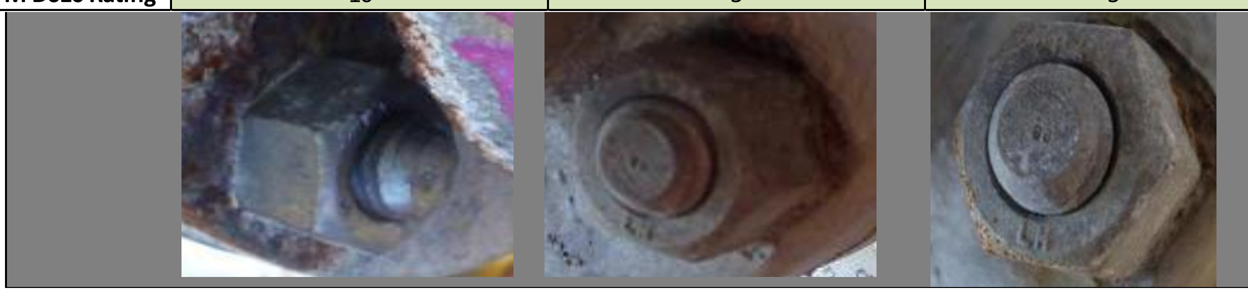

Figure 12: Field Trial Time Progression: Nanolaminate Zinc-nickel 1

Zn-Ni Nanolaminate 2			
Monitor Date	14-Jul	15-Jul	16-Jan
Months in Service	12	24	30
Total Red Rust %	0%	0%	0%
ASTM D610 Rating	10	10	10

Figure 13: Field Trial Time Progression: Nanolaminate Zinc-nickel 2

ANALYSIS AND DISCUSSION

Figure 14 (below) shows the modified D610 rating after 30 months of exposure for every fastener in the trial by coating type.

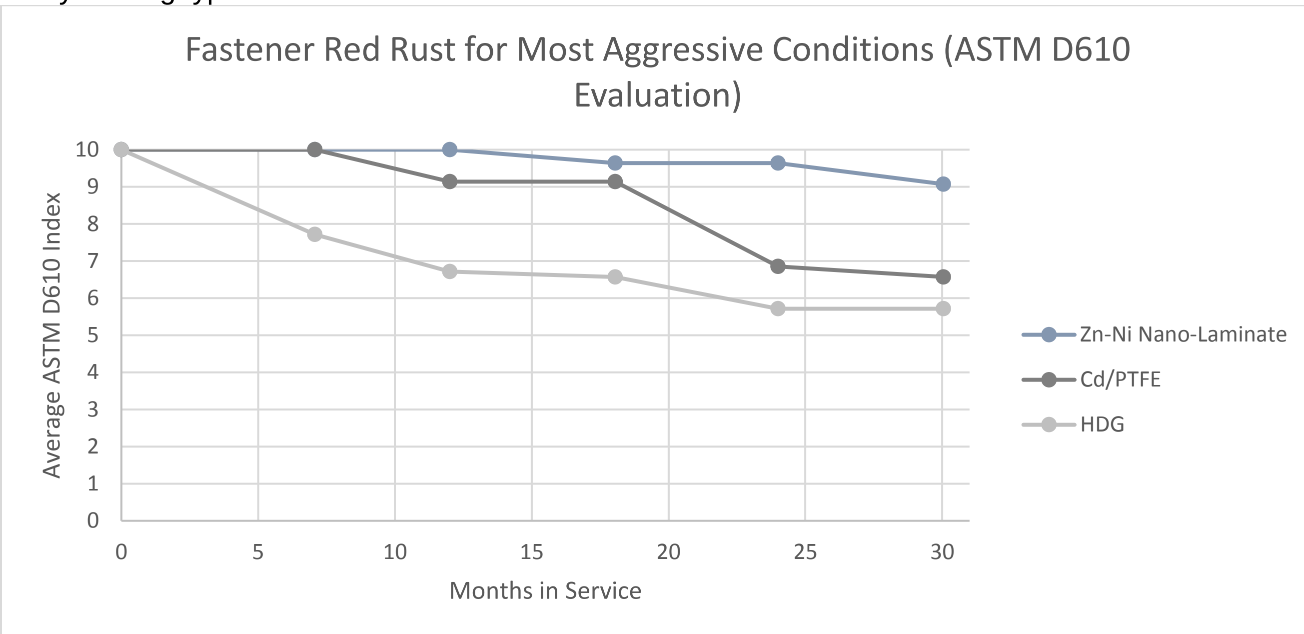

Figure 14: Average D610 grade for each coating type.

For comparison, Figure 15 (below) charts the average % red rust rankings for the same series of trials. While the relative performance is more conservative in the case of the D610 analysis (more aggressive up to 1% red rust, less aggressive through 3-5% red rust), the relative performance is nonetheless consistent, indicating that the index-based rating approach is appropriate for systematic field evaluation of corrosion.

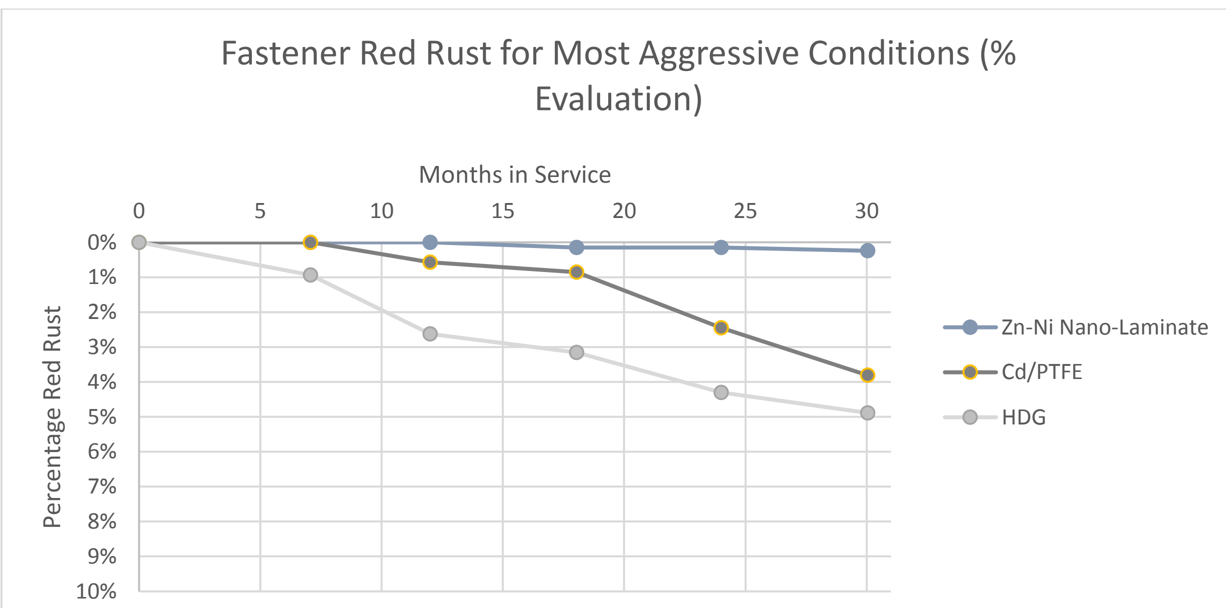

Figure 15: Average % red rust for each fastener coating type

Figures 16 and 17 (below) show the modified D610 rating of fasteners evaluated in ASTM B117 salt fog environment, again, we see here the expected relative performance of the various fastener types

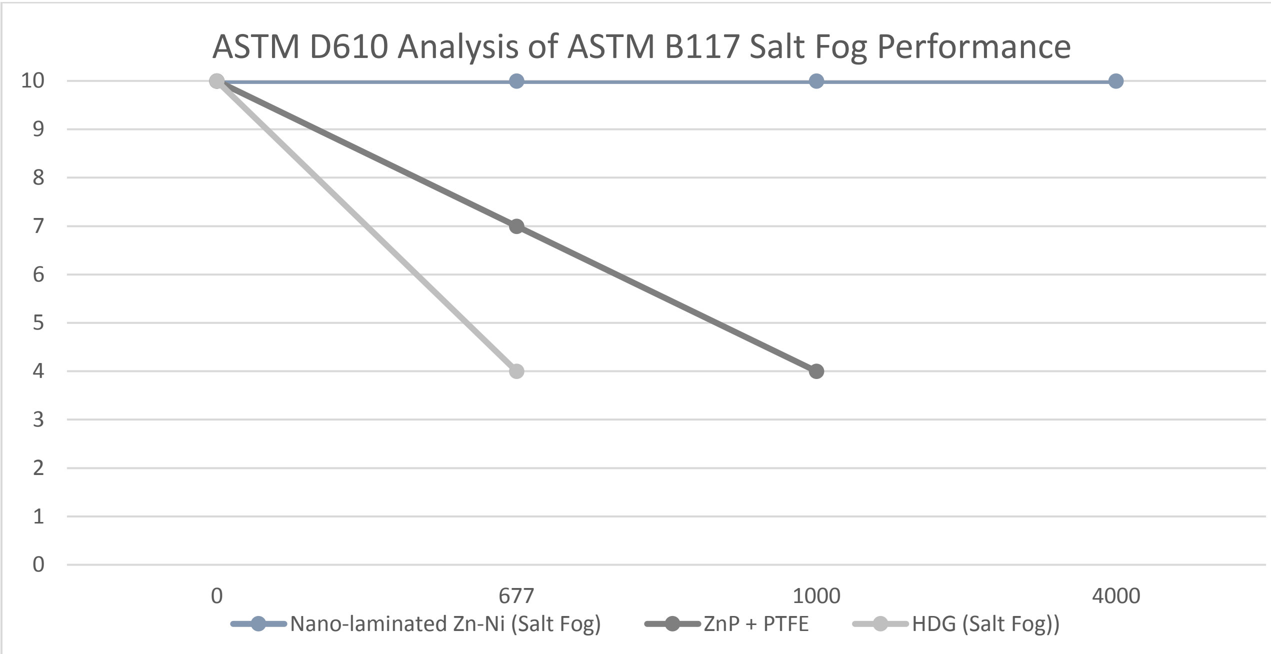

Figure 16: Average D610 grade for each coating type during salt fog exposure

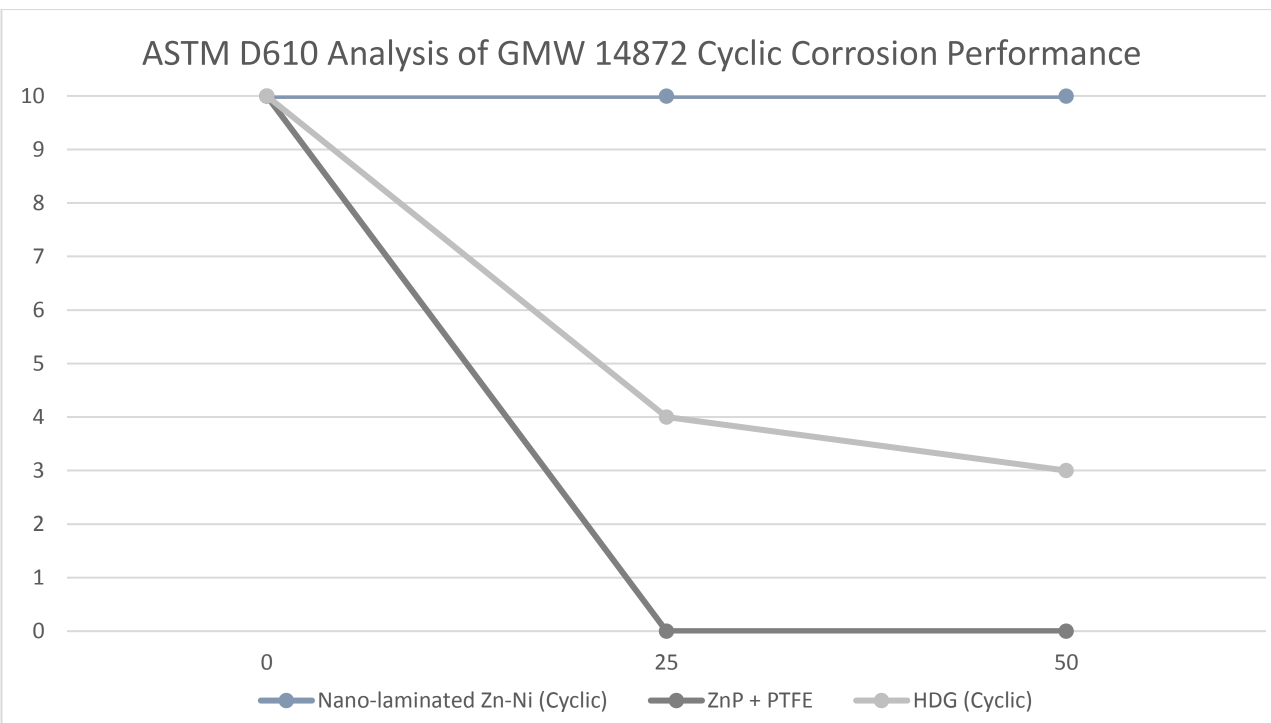

Figure 17: Average D610 grade for each coating type during cyclic corrosion exposure

CONCLUSIONS

Comparison of the percentage red rust reported by visual observation and by the modified D610 analysis (described in this paper) shows good promise for use in evaluating the degree of corrosion on fasteners both in laboratory tests and in field conditions. The ASTM D610 based fastener evaluation methodology described in this paper provides a consistent red rust reference that minimizes the subjective observations typical of laboratory and field trial evaluations of coating performance. Utilizing this modified D610 method to evaluate the results from repeated inspections provides a means to compare performance of fastener coatings.

Evidence across numerous lab-based tests and field trials have demonstrated that the zinc-nickel nanolaminate coating provides significantly better fastener corrosion protection than conventional coating systems.

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