ZNnGard™ Pulse Plated Nanostructured Zinc-Nickel: Engineered Bolting for Offshore Oil & Gas

Coating system for Oil and Gas Industries Designed to replace cadmium, PTFE & ceramic-metallic coatings

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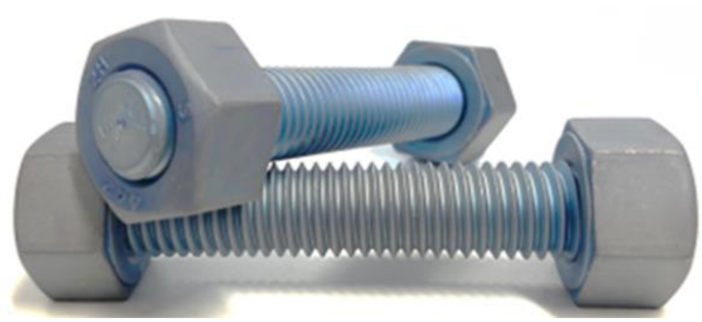
ZNnGard™ \\`zen·gärd\\
A Zinc-Nickel nanostructured electroplating system that is considered part of an overall strategy to replace cadmium, PTFE, ceramic metallic, and fluoropolymer processes, eliminate environmental and worker safety issues while significantly improving performance and reducing life-cycle costs.



Need for Corrosion Protection of Fasteners on Offshore Platforms

According to the Bureau of Safety and Environmental Enforcement (BSEE) and the Bureau of Ocean Energy Management (BOEM), there are over 1800 and 2000 Oil & Gas offshore platforms and Coastal facilities, respectively, in the Gulf of Mexico alone. Steel fasteners are used extensively throughout these platforms and serve critical roles on numerous components including pressure boundary and wellhead control devices. The likelihood of a fastener failure is directly related to both the mechanical strength of the fastener in the operational environment and the service range stresses, neither of which remain constant over time due to the highly corrosive environment of the offshore platform. To prevent corrosion-related failures, critical bolting is inspected, replaced, and maintained on annual schedules. Currently, over 70% of the bolting is replaced every year on-board an average offshore platform. Six offshore platforms owned by one major integrated oil and gas company uses over 175,000 lbs of carbon steel fasteners annually. There is a need to increase the lifespan of bolting to minimize the frequency of their replacement, saving cost and downtime. In this whitepaper, ZNnGard™ is shown to be an ideal solution to improve the corrosion performance of high pressure steel bolting used in valves, flanges, piping, etc.

What is currently used… Conventional Corrosion Protection Coatings

Conventional corrosion protection coatings improve the corrosion resistance of a steel fastener and can often be grouped into two categories: barrier coatings and sacrificial coatings. Barrier coatings often have very high corrosion resistance and protect the steel by providing a physical barrier between the steel and the corrosive environment. Sacrificial coatings, as the name implies, will preferentially corrode while cathodically protecting the underlying steel substrate, but they are limited to certain metals that act as the galvanic anode when coupled to steel (e.g., Zn, ZnNi, Al). Sacrificial coatings have the added benefit of being able to protect the steel even when there is a breach in the coating (e.g., from scratches, bolt

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torqueing, holidays/defects in the coating during application); as such, they can often provide superior protection in aggressive environments.

Cadmium-plated studs & nuts were used extensively in the 1970s to late '80s and provided good corrosion resistance, serving as a sacrificial coating with good lubricity and a relatively long-life span. Cadmium, however, is a toxic heavy metal, which is harmful to human health. The Environmental Protection Agency lists Cd as a probable human carcinogen (class B1)[1], and strictly regulates the emissions of Cd to the atmosphere and the disposal of Cd and Cd-containing wastes. In addition, cadmium is not biodegradable, which means it can remain in the environment for a long time after it is released, causing long-term damage to the ecosystem. The potential for bioaccumulation of cadmium in marine environments is a concern and can result in high concentrations in the tissues of marine life, such as fish and other animals, if not properly managed.

Over the last few decades, the oil and gas, aerospace, and defense industries have investigated multiple Cd-alternate coating technologies for steel fasteners, with some of the most promising concepts starting to see some acceptance in various military and commercial Cd-replacement roles. However, to date there is no universal solution. Zinc (galvanized or electroplated) and Zinc-Nickel (electroplated) are two of the most promising alternatives, often finished with a topcoat (e.g., chromate conversion coatings, fluoropolymer). Fluoropolymer topcoats are barrier coatings that provide low friction and consistent torque, but the coating can be easily damaged by torquing during installation. One of the major disadvantages of fluoropolymers, however, is their environmental persistence. These materials do not break down easily in the environment and can accumulate in the food chain, potentially leading to health problems for wildlife and humans. Additionally, the production of fluoropolymers can release perfluorinated compounds (PFCs) into the air, which can be harmful to human health and the environment. Because of these concerns, the use of fluoropolymers has come under increased scrutiny in recent years.

Like Cadmium, traditional direct current (DC) electroplated Zinc & Zinc-Nickel coatings act as a sacrificial coating to protect the steel. Due to the more active nature of Zinc coatings (larger potential difference between Zinc and steel), they corrode more quickly than Cadmium and require frequent bolting replacement. DC electroplated ZnNi has been identified by several groups as offering a set of properties that make it promising as a Cd alternative. However, one of the shortfalls[2] is related to the potential for hydrogen embrittlement and re-embrittlement of high-strength steels during exposure to a corrosive environment such as salt water, which is an environment of particular interest for the U.S. Navy, (specifically for critical load-bearing components such as wheels and landing gear) and for offshore oil platforms with the use of high strength steel fasteners. To alleviate the issues with hydrogen embrittlement, DC plated Zinc-Nickel formulations have been created with intentional porosity to allow the hydrogen that is generated in the plating process to escape during post-plating hydrogen relief baking. The resulting porous coating, however, was found to result in questionable hydrogen re-embrittlement performance if the ZnNi coating did not have a subsequent polymeric top-coat. DC plated Zinc-Nickel coatings have also been found to have higher torque values required to achieve the same tension values as cadmium due to the higher roughness associated with the porous nature of the coating.

Ceramic-metallic coatings followed by a fluoropolymer topcoat is also a common alternative but is also beginning to decline in use. This system has better corrosion resistance and a consistent friction effect; however, the ceramic coatings are thick (>1 mil) and require oversized nut tapping to accommodate the coating thickness.

At the direction of BSEE, the industrial standards that set the requirements on allowance and tolerance of the bolt & nuts threads have recently changed. The American Petroleum Institute Standard API-20E, "Alloy and Carbon Steel Bolting for Use in the Petroleum and Natural Gas Industries" specifies that "Oversizing of nut threads or under-sizing of bolt threads is not permissible." However, ASME B1.1 Unified Inch Screw Threads Class 2A fit (B1.13M Class 6g fit Metric) specifies, "Unless otherwise specified, size limits for standard external thread Class 2A apply prior to coating. The external thread allowance may thus be used to accommodate the coating thickness on coated parts, provided that the maximum coating thickness is no more than one-fourth of the allowance." While the ASME standard is accepted, it directly contradicts the API specification and the BSEE guidelines. Regardless, a corrosion coating system that does not require the use of oversized nuts is preferred.

ZNnGard™: Nanostructured ZnNi for Cd Replacement – Ideal for Steel Fasteners & Bolts

Recognizing the need to replace cadmium on fasteners and a range of manufactured components, Strategic Environmental Research and Development Program (SERDP) funded a program with Integran Technologies Inc. on cadmium replacement using electrodeposited nanocrystalline Zinc-Nickel alloy coatings. SERDP project WP-1616 investigated the use of pulse plating to obtain a fine-grained microstructure using different Zn-based electroplating chemistries for potential Cadmium replacement. Through this work, a new electroplated ZnNi alloy was developed utilizing pulse plating of an alkaline-based plating chemistry that provided excellent performance with a clear benefit from using pulse plating compared to traditional DC plating.

[1] http://www.epa.gov/ttn/atw/hlthef/cadmium.html (accessed February 2012).
[2] For example, see USAF/ES3/Boeing Presentation, "Low Hydrogen Embrittlement (LHE) Zinc-Nickel (Zn-Ni) Qualification Test Result and Process Parameters Development," (9 February 2011).

The fine-grained structures produced via pulse plating from modified commercial ZnNi-alloy plating solutions were found to have a number of benefits over conventional DC plating, including bright, uniform, dense microstructures; uniform, equiaxed grain size throughout the thickness of the coating; increased microhardness; single γ-phase crystallographic microstructure; increased corrosion resistance compared to other Zn-Ni alloys; and decreased friction. They also passed the ASTM F519 hydrogen embrittlement (HE) test. ZnNi coatings synthesized from alkaline bath chemistries had greater compositional uniformity (less fluctuation with variations in current density) compared to those from acid chemistries, resulting in more uniform peak to valley composition in threaded fasteners. In addition to providing dense structures, pulse plated deposits typically possessed higher nickel content than DC plated deposits from the same plating bath. Both Cr^{6+} and Cr^{3+} conversion coatings were successfully applied to the pulse plated ZnNi structures, providing similar enhancement to salt spray corrosion performance. The ability to pass the HRE test was highly dependent on the following factors: pre-plating treatment methods, porosity of coating, nickel content, and the open circuit potential (OCP). Finally, bulk processing of large numbers of fasteners was successfully accomplished using pulsed electrical parameters while barrel plating.

Sigma Fasteners believes that pulse plated Nanostructured Zinc Nickel coated fasteners will gain wide acceptance as the long-sought replacement for cadmium plated bolts and PTFE formerly used in Oil and Gas industries worldwide, and recently licensed the pulse plated Nanostructured ZnNi technology from Integran Technologies. Dipsol America is the master distributor for the expressly branded ZNnGard™ chemistry and components for plating and chromate finish for use in the oil and gas sector. A ZNnGard™ production line for rack and barrel plating steel fasteners has been installed at Sigma Fasteners' facilities in Houston, Texas.

Figure 1 shows optical micrographs of a cross-section of conventional DC electroplated ZnNi coated onto steel (left image) and compares it to pulse plated ZNnGard™ coated onto steel (right image), both coatings produced using the same alkaline bath chemistry. The use of the pulse plating waveforms with the alkaline ZnNi plating system led to a uniform dense microstructure compared to the porous microstructure that resulted with DC plating. Due to the high diffusivity of hydrogen through the nanocrystalline grain structure, the dense microstructure does not cause hydrogen embrittlement issues, and all test samples passed ASTM F519 hydrogen embrittlement testing; this is a different mechanism to relieve hydrogen compared to conventional DC electroplated ZnNi that relies on its porous microstructure. The resulting dense microstructure also provides superior protection to hydrogen re-embrittlement (a.k.a. in-service embrittlement), by reducing the probability of hydrogen diffusing into the steel substrate during active corrosion. Resistance to hydrogen re-embrittlement is particularly important as it is a critical parameter with which to evaluate the practical use of high-strength steel fasteners; and it is a difficulty with many of the current cadmium-replacement alloys. The uniform fully-dense nanocrystalline microstructure also improves hardness, wear resistance, lowers the friction coefficients, and provide improved aesthetics.

Corrosion Protection of Steel using ZNnGard™

ZNnGard™ provides excellent corrosion protection of steel fasteners and bolts in Offshore Oil & Gas environments, prolonging their in-service life. The corrosion performance is attributed to its microstructure and composition (uniform, dense, nanostructured, single γ-phase). ZNnGard™ acts as a sacrificial coating to steel, protecting the steel even if the coating is damaged due to its lower (more negative) OCP compared to steel (ZNnGard™ acts as the anode, preferentially corroding while the steel acts as the cathode and is protected).

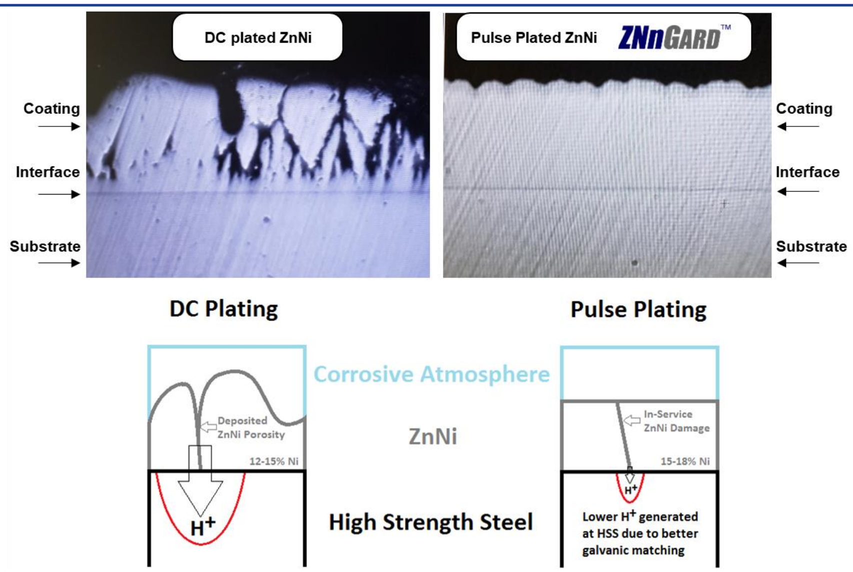
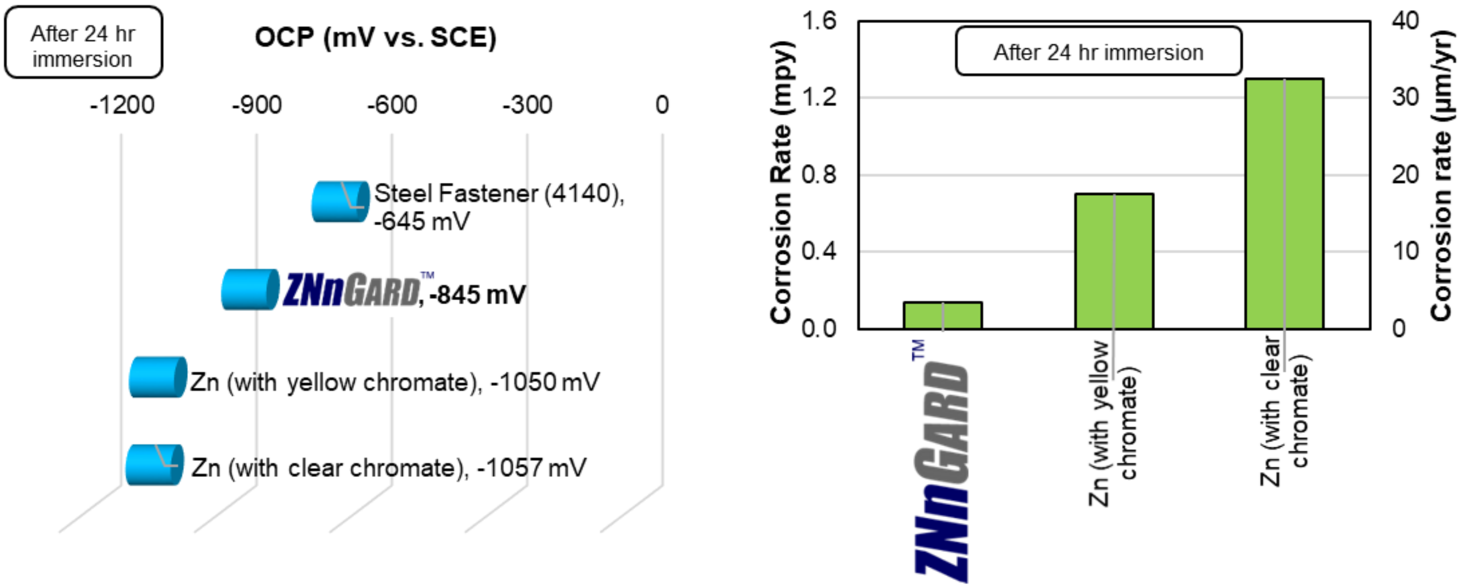


Figure 1: *Optical micrograph of a conventional DC electroplated ZnNi coating on steel (top left) and a pulse plated ZnNi (ZNnGard™) coating on steel, synthesized from the same Alkaline bath chemistry. A schematic (bottom) illustrating how porosity in a ZnNi deposit can increase the probability of Hydrogen diffusing into the steel substrate during corrosion*



Aqueous electrochemical testing was performed in 5 (w/w) % NaCl solution at 25°C (naturally aerated and stagnant). The potential was measured using a saturated Ag/AgCl reference electrode and potentials were converted relative to a saturated Calomel electrode (SCE). Both open circuit potential (OCP) and corrosion rate measurements were taken after 24 hours of immersion. The corrosion rate was determined using polarization resistance (ASTM G59).

Figure 2: *The corrosion performance of ZNnGard™ is compared to other materials showing the OCP (left) and corrosion rate (right). ZNnGard™ includes a trivalent chromate topcoat.*

Figure 2 provides a comparison of the OCP of ZNnGard™ (including a trivalent chromate topcoat) and some other coatings in a salt water (5% NaCl); the OCP is commonly used as a method to predict the galvanic corrosion effects of materials (in this case a lower OCP than steel is required for cathodic protection). As show in Figure 2, ZNnGard™ has a lower OCP than steel, but not as low as conventional Zinc coatings; this is preferable since the smaller OCP difference reduces the polarization of steel when exposed through the coating (lower driving force for hydrogen re-embrittlement of the steel). ZNnGard™ is also shown to have an order-of-magnitude lower corrosion rate than conventional Zinc in aqueous salt water (Figure 2), suggesting a longer lifespan of ZNnGard™.

The corrosion protection of steel using ZNnGard™ (including a trivalent chromate topcoat) was demonstrated using salt spray testing following a modified ASTM B117 procedure, with the results shown in Figure 3. Figure 3 presents 3 sets of salt spray testing data. The top data set in Figure 3 compares the scribed salt spray performance of steel Q-panels coated with ZNnGard™ to those electroplated with conventional Zinc coatings (with trivalent chromate); ZNnGard™ outperforms the conventional Zinc coatings with ZNnGard™ showing no indications of red nor white rust. The middle data set in Figure 3 shows the long-term salt spray corrosion performance of scribed ZNnGard™ coated steel panels; no red rust is observed even up to ~7200 hours. Finally, the bottom data set in Figure 3 presents the salt spray testing of ZNnGard™ coated steel bolts that showed no red rust up to ~8000 hours.

Summary

ZNnGard™ is a dense, nanostructured ZnNi alloy coating that is produced via pulse electrodeposition using an alkaline Zn-Ni bath chemistry, and can lead to the retention of numerous benefits associated with Cd-coating technology, including non-line-of-sight application, excellent corrosion resistance, low coefficient of friction, excellent coating adhesion, high dimensional consistency, and superior surface finish. The use of pulse plated ZNnGard™ was also found to have benefits over conventional DC ZnNi electroplating plating, including superior corrosion protection and improved HRE performance. Pulse electrodeposition can be implemented within the existing Cd-plating infrastructure for conventional rack plating as well as bulk plating of fasteners, e.g., barrel plating.

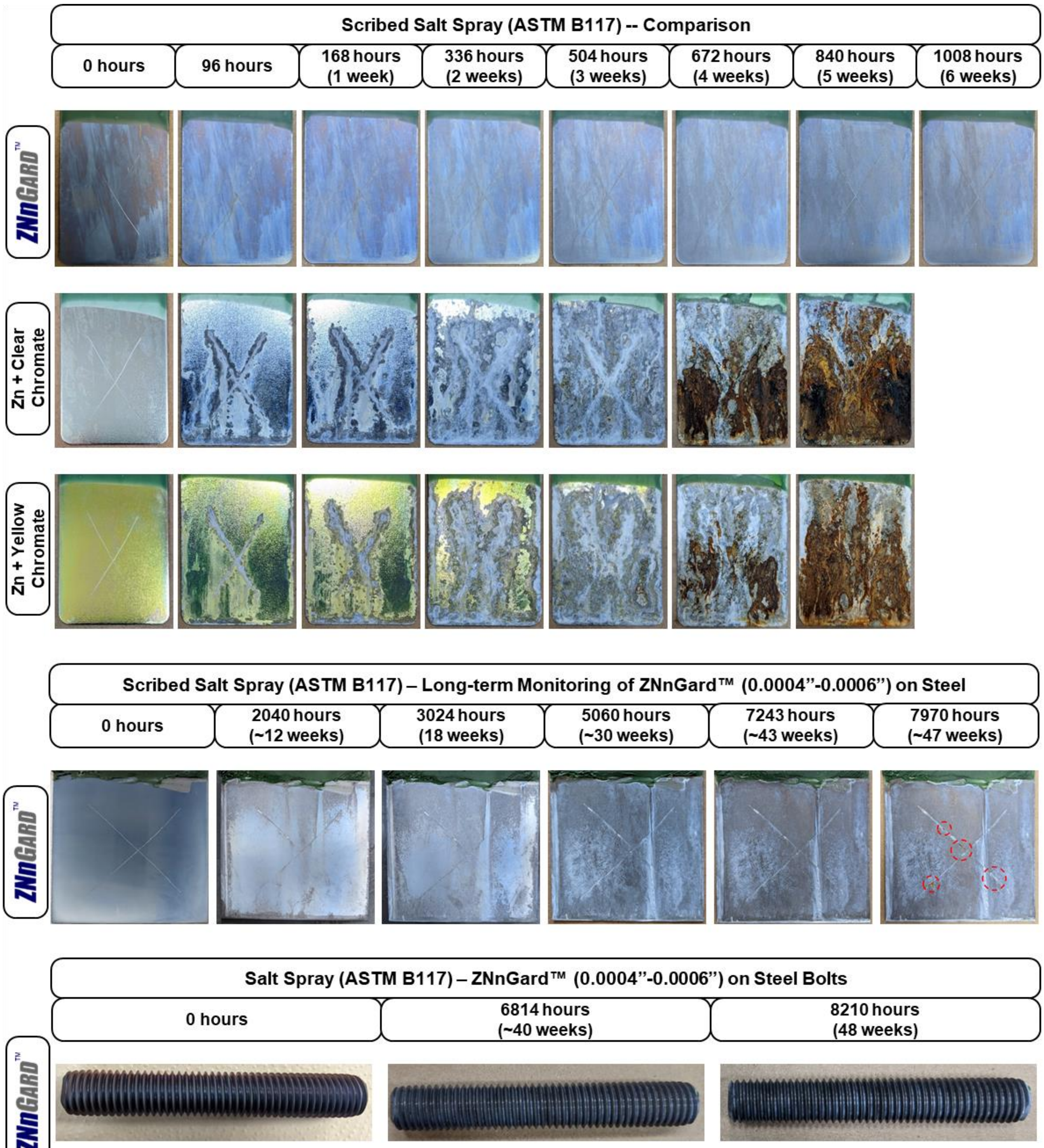


Figure 3: *The salt spray (ASTM B117) corrosion performance of ZNnGard™ coated steel panels is compared to conventional electroplated Zn with either a Clear or Yellow Chromate coating (top set of images). ZNnGard™ includes a trivalent chromate topcoat. Samples were scribed prior to testing using a Lathe Tool Type as per ASTM D1654. Salt spray testing was monitored for up to ~1000 hours showing no red rust nor white rust on ZNnGard™, while the Zn samples showed extensive white and red rust. Long-term salt spray performance of ZNnGard™ (middle set of images) and ZNnGard™ coated onto a steel bolt (bottom set of images) are also provided.*

About the Authors

Sigma Fasteners, Dipsol, and Integran have worked together to bring the Nanostructured Zinc Nickel coating system to the Oil and Gas Industries. ZNnGard™ meets the requirements of the ASTM B841 Class 2 as an electrodeposited zinc-nickel alloy coating on fasteners. Integran Technologies is the master licensor for its Nanovate™ Zn-Ni Technology and intellectual property owner in waveform pulse plating technologies. Dipsol America is the master distributor for the expressly branded ZNnGard™ and ZNnCoat™ chemistry and components for plating and chromate finish. Sigma Fasteners, a leader in Energy bolting, will utilize this expertise in converting our current Zn-Ni line to meet Integran standards and Dipsol chemistries to ramp up advanced field testing and production in Houston.

Integran is a world leader in advanced metallurgical nano-technologies, providing a broad international base of customers with advanced process & product design solutions through R&D, material sales, contract manufacturing, and technology licensing. Integran has been at the forefront of metallurgical nanotechnology development for over twenty years and has established an international reputation for excellence in materials technology development and commercialization. Integran owns the intellectual property rights for the cost-effective production of metallurgical nano-structures with over 250 patent filings dealing with the structure, composition, processing, and application of its revolutionary materials.

Dipsol was founded in 1953 with the aim and focus of establishing a "comprehensive" manufacturer of metal surface finishing products. In November of 1965, the Dipsol technical research team launched a noncyanide zinc plating brightener technology which was the FIRST in the world to introduce the commercial application. Dipsol also successfully developed and introduced commercially neutral Tin, Tin/Zinc and pioneered the Zinc-Nickel alloy plating processes. Since 1989, Dipsol of America has manufactured and serviced many metal finishing products, including zinc, zinc alloys, topcoats, passivation, and other surface finishing chemicals. Headquartered in Livonia, Michigan, Dipsol of America operates from a state-of-the-art facility that includes testing, failure analysis, and analytical equipment, and educated technical and support staff.

Sigma Fasteners, Inc. provides industry-leading knowledge in manufacturing, corrosion control, and distributing critical engineered high-pressure bolting, supporting the world's energy transition while striving to achieve operational excellence, helping our employees and their communities while protecting the planet. Sigma holds an American Petroleum Institute API 20E-0017 Monogram to manufacture API 20E bolting, API 20F-0007 Monogram, and is certified API Spec Q1, 9th edition. Sigma distributes standard bolting and manufactures critical bolts meeting industry specifications, customer specifications to current revisions, and per print. Sigma is ISO 9001:2015 certified and is on the approved vendor list of major wellhead manufacturers, energy OEMs, and petrochemical companies worldwide.

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