FINAL REPORT

Environmentally Friendly Anticorrosion Coating for High Strength Fasteners

SERDP Project WP-1617

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PPG Industries, Inc.

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Alternatives to both processes have been pursued with very promising results. This work describes a multi-layer approach to provide a protective coating system. These systems include a sacrificial metal base coat and may also include an organic topcoat technology that will provide the best combination of corrosion resistance and barrier properties. These approaches impart high end s

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Keywords: zinc rich, fasteners, electrodeposition, dip-spin, inorganic coating, cadmium replacement

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ACRONYMS

AISI	American Iron and Steel Institute
ARL	Army Research Lab
ASETSDefense	Advanced Surface Engineering Technologies for a Sustainable Defense
ASTM	American Society for Testing and Materials
COF	Coefficient of Friction
CRS	Cold Rolled Steel
DOD	Department of Defense
E-Coat	Electrodeposition Coating
ESTCP	Environmental Security Technology Certification Program
EZG	Eloctro Zinc Galvanized
GM	General Motors (Corporation)
HDG	Hot Dip Galvanized
NACE	National Association of Corrosion Engineers
NAVAIR	Naval Air Systems Command
NAVSEA	Naval Sea Systems Command
Nm	Newton Meters
NSPR	Naval Surface Preparation and Repair
OCP	Open Circuit Potential
OEM	Original Equipment Manufacturer
PACE	Paint and Coatings Exposition
SERDP	Strategic Environmental Research and Development Program
ZRC	Zinc Rich Coating

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ABSTRACT

There exists a need for environmentally benign coatings to eliminate cadmium and/or chromate containing coatings on high-strength fasteners. These alternative replacement coatings would provide high-strength, corrosion resistant fasteners for use in weapon systems. Traditionally, high-strength steels have been used with cadmium (Cd) electroplated coatings, followed by a hexavalent chromium (Cr^{6+}) rinse. The environmental and human health hazards associated with both cadmium and chromates are well established. The elimination of hazardous materials will improve the life cycle costs and environmental / occupational health issues associated with the manufacture and maintenance of DoD weapon systems.

Alternatives to both processes have been pursued with very promising results. This work describes a multi-layer approach to provide a protective coating system. These systems include a sacrificial metal base coat and may also include an organic topcoat technology that will provide the best combination of corrosion resistance and barrier properties. These approaches impart high end sacrificial corrosion resistance properties without use of hazardous Cr or Cd and without hydrogen embrittlement of fasteners.

Keywords: zinc rich, fasteners, electrodeposition, dip-spin, inorganic coating, cadmium replacement

OBJECTIVES

The objective of this work is to develop new environmentally benign coating technologies that could possibly eliminate the need for cadmium or chromate coatings on high-strength fasteners. These technologies would provide a coatings system for high-strength, corrosion resistant fasteners for use on both legacy weapon systems and new weapon platforms. The key performance criteria for these coatings are as follows:

Toxicity – The coating system must be free of toxic components including cadmium, chromium (6+), and lead.
Corrosion Resistance – Screening will be done using ASTM B117 Salt Spray. Coated fasteners must withstand a minimum of 1000 hours with no apparent red rust spots.
Coating Thickness – Since threaded bolts must mate with a corresponding threaded receptacle (e.g. nut), the film thickness of the total coating must not exceed 20 microns. Bolt/nut pairs must be easily assembled by hand without binding.
Torque/Tension – Screening for adequate lubricity will be done using the General Motors specified test bolts and method (GMW3359, Ford WZ101 110607). The coating must perform equal to a cadmium plated control.
Hydrogen Embrittlement – The coating must not cause direct hydrogen embrittlement as measured by ASTM F519 1a.1 test method.
Application – The coating materials must be stable and able to be applied using conventional, existing commercial methods such as dip-spin, dip-drain, spray, and electrodeposition.

BACKGROUND

Traditionally, high-strength steel fasteners have been used with cadmium electroplated coatings followed by a hexavalent chrome rinse. The environmental and health hazards associated with cadmium and hexavalent chromium are well established[1,2] and significant legislation has been put in place recently to limit their continued usage[3,4]. It is critical that suitable replacement technologies be identified that can provide these high performance characteristics in a cost effective manner.

There are a variety of coating systems commercially available which have been used for many years in the automotive, industrial, and construction industries. The non-toxic alternatives include zinc and nickel plating, zinc flake dip-spin primers, dip-spin organic topcoats, and electrodeposition topcoats. While zinc/nickel plating offers substantial corrosion protection, it is costly and suffers from the same possibilities of hydrogen embrittlement as does cadmium plating[5,6]. In addition, plated surfaces can be problematic for adhesion of topcoats. Similarly, conventional dip-spin zinc flake primers are difficult to topcoat. Adhesion can be poor and corrosion performance (with topcoat) is inadequate.

Conventional zinc rich coatings are inadequate for use in fastener applications for several reasons. The majority utilize zinc dust, which is spherical in geometry. In thin film applications, there is not enough zinc surface area or metal contact for true sacrificial activity[8] (Figure 1). Binders used in conventional primers are either organic resins, such as epoxy, or inorganic silicates[7,9]. The organic resins tend to insulate the zinc and disrupt electrical contact necessary for sacrificial performance. Silicates are often used as binders but are very brittle and generally not stable enough in a single component to be useful in a continuous dip-spin type application.

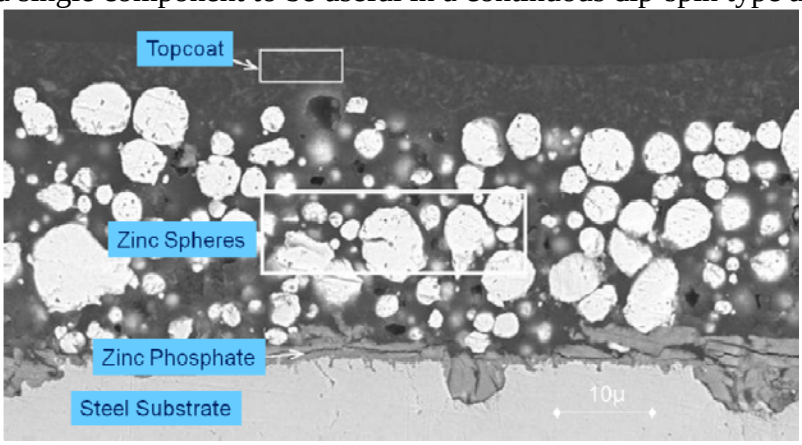


FIGURE 1 – Zinc Dust Primer Cross Section

Topcoats for fasteners are generally applied either by conventional dip-spin methods, or by the electrodeposition process. In terms of suitability for application, electrodeposition coatings offer the best coverage and performance. This is a superior method of applying an even film thickness in a single coat, on complex parts such as a barrel of small parts or fasteners. The combination of zinc phosphate pretreatment plus cationic epoxy electrodeposition topcoat has been used commercially for several years. Electrodeposition is also a very environmentally friendly process. The drawback, however, is that this finish offers only about 250 hours of salt

spray resistance before appearance of red rust spots, when used without a zinc rich primer. In addition, there can be significant capital cost for installation of a new electrodeposition line.

Electrodeposition Process

In general the process of electrocoating consists of an electrically conductive substrate submerged into a water based paint bath, electricity is applied to the part and the charged particles are deposited onto the substrate.

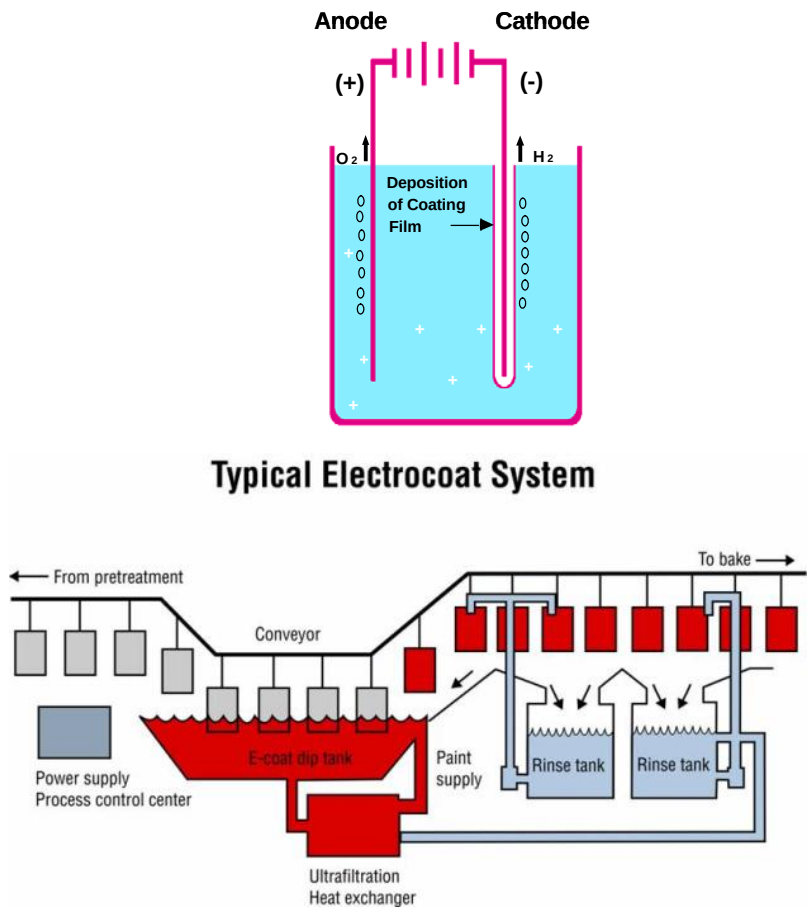


FIGURE 2 – Cathodic Electrodeposition

As depicted in Figure 2, the electrocoat process starts after the part is conveyed from pretreatment. The part enters into the electrocoat bath where a charge is applied, current distributes through the part and coating begins to take place. The coating process operates on the basis of hydrolysis of water. In the cathodic system, a basic environment is generated at the interface of the substrate. This causes the paint to precipitate onto the part. As the deposition continues film thickness on the part increases. Film thickness of the coating can be controlled by manipulating temperature of the bath, amount of voltage applied, or coating deposition time. Due to the nature of electrocoat the deposited film is inherently self limiting. This means that the film will eventually insulate so that coating is redirected to bare areas of the part. This process is

called throwpower and this is what gives electrocoat many advantages over standard spray, powder or dip applications. This property is most advantageous on complex shaped parts.

TECHNICAL APPROACH

In this work we proposed a multilayer coating system (Fig 3) consisting of a conventional zinc phosphate pretreatment followed by a zinc flake based primer, then a cationic electrodeposition topcoat. Additionally a silver aluminum based topcoat was developed for application where electrodeposition equipment was not available. The bulk of the work was focused on development of novel inorganic binders and novel zinc flake technology for the sacrificial zinc primer. This primer is superior over current zinc rich primers for corrosion performance and adhesion when used with the cationic electrodeposition topcoat. The topcoats were formulated for adequate torque/tension performance and color variations.

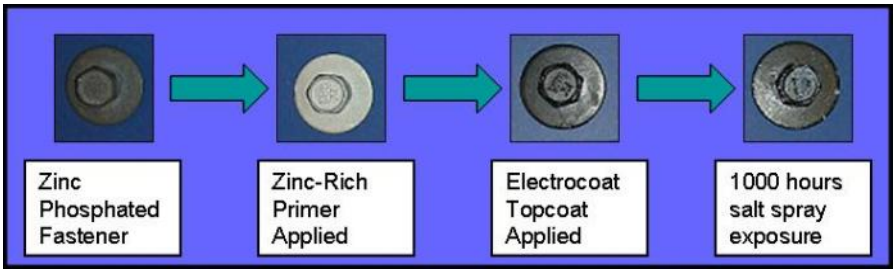


FIGURE 3 - Multilayer Coating Process and Corrosion Screening

Substrate Preparation / Pretreatment

Several methods were tested for preparation of the test substrate. The raw fasteners as received from the manufacturer are treated with an oil to prevent rusting prior to coating. All were cleaned with a conventional caustic cleaner to remove the oil and scale. Both flat cold rolled steel panels and steel fasteners were tested with treatments as follows:

A. Zinc Phosphate 1 – Medium crystal size Zn phosphate (Irco Bond® Z24, PPG Industries)
B. Zinc Phosphate 2 – Fine crystal size Zn phosphate (Chemfos® C700-C59, PPG Industries)
C. Zirconium Treatment 1 – Zircobond® 4200 (PPG Industries)
D. Zirconium treatment 2 – X-Bond® 4000 (PPG industries)
E. Grit Blast
F. Cadmium Plate with Chromium 6+ rinse (DeTray Plating)

Fasteners – M10 Grade 10.9 test bolts (Wilson Gardner Co.)
Panels – 24 gauge bare cold rolled steel (Q-Panel Co.)

The test specimens were coated with a zinc rich primer by dip-spin for an average film thickness of 0.3 mils., and topcoated with cationic electrocoat (Powercron XP) for a total film thickness average of 0.7 mils. Experimental control is Cd/Cr+6 plate.

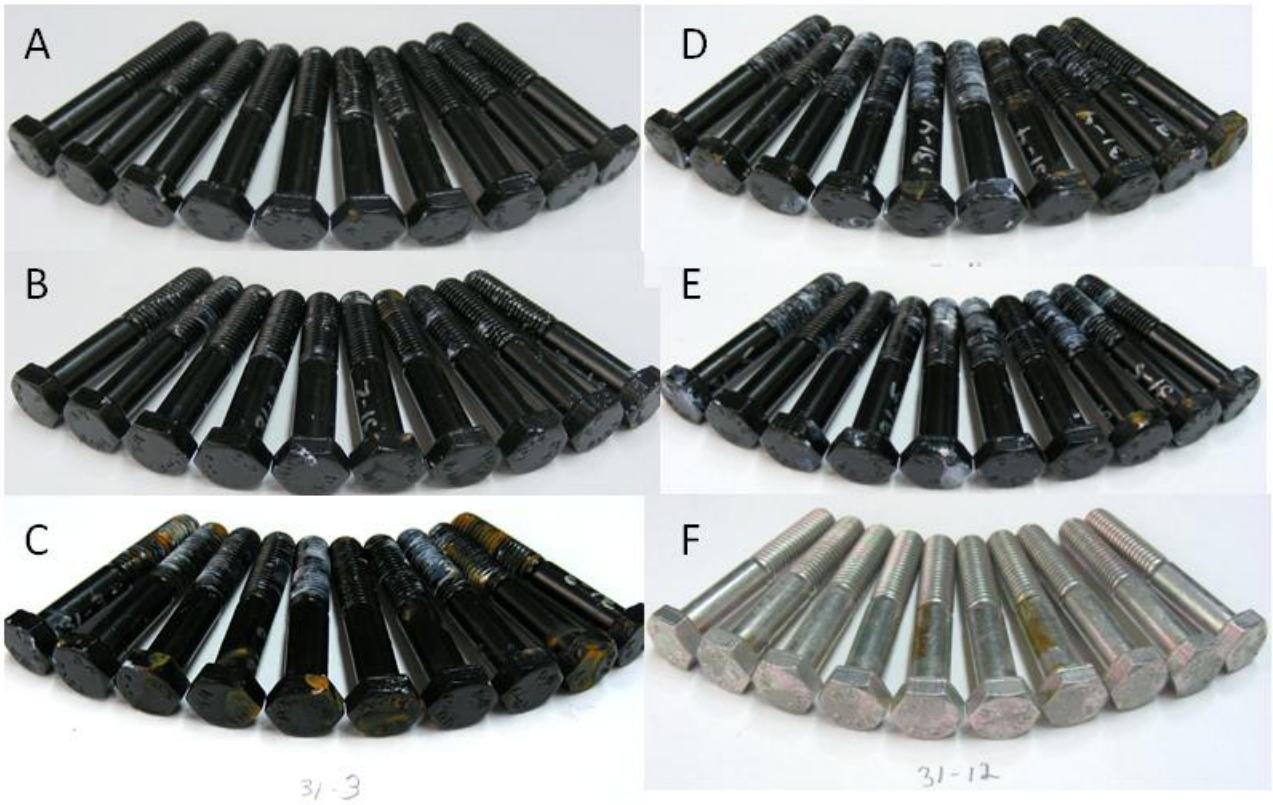


FIGURE 4 – Test Bolts – 1000 Hours B117 Salt Spray – Pretreatment Variations

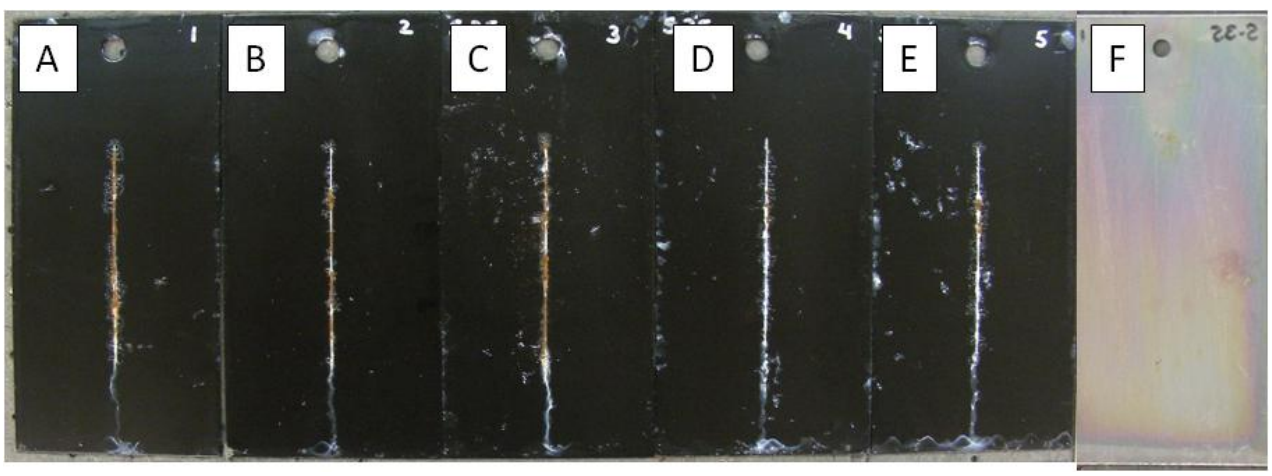


FIGURE 5– Flat Panels – 500 Hours B117 Salt Spray – Pretreatment Variations

Figure 4 illustrates the corrosion results after 1000 hours of Salt Spray exposure for sets of ten industrial grade hex bolts. Figure 5 shows 500 hours of Salt Spray exposure for flat cold rolled steel panels, each with a three inch scribe line down to bare steel. The samples were rinsed with deionized water after exposure. Both red and white corrosion is evident.

The results show that the two zinc phosphate variations give the best results, especially on the test bolts. There are only a couple of minor pinpoints of red rust evident. The degree of white corrosion and blistering is less for these as well. In comparison, the grit blasted samples

(E) show much more white corrosion and several large red rust spots. Both zirconium based treatments showed unacceptable red rust.

The flat panel samples show less white corrosion and significantly less face blistering for the zinc phosphate treatments. However, it is clear that the scribe line on panels is a much larger damage area than a "touch point" on a fastener. Therefore there is some degree of red rust in the scribe on all of the panels. Variants D and E show the most white corrosion, therefore tend to show less red rust in the scribe. For this reason, we feel that flat panel testing does not correlate well with fastener testing.

In both sets, the cadmium plated controls showed no failure.

Past conventional thinking indicates that grit blasting is a requirement for sacrificial zinc coatings[9]. Although zinc phosphate is an insulating material, the crystal structure is porous. We theorize that there is sufficient contact between the zinc metal flake and the iron substrate through the zinc phosphate for sacrificial activity.

Based on these results, we conclude that zinc phosphates, large or fine crystal, are most suitable for this coating system. Both of these phosphate types are commercially available and in use by fastener coating applicators in North America.

Zinc Rich Primer – Binder Development

The new proprietary zinc-rich binder technology replaces conventional silicate chemistry with analogous organotitanate technology. Like silicates, the titanates cure by hydrolysis and pyrolysis of the organotitanate to form titanol species which subsequently condense to form a titania matrix. Titanates, however are more reactive that the silicate analogues and are capable of reacting with organics as well as by self-condensation[10]. This offers the opportunity to easily form organotitanate hybrid binders with greater flexibility and rheology control. Organotitanates are of the general formula $Ti(OR)_4$. Where the -OR group can be a wide variety of organic moieties. The organic group can be chosen to provide the proper balance of cure rate, hydrolytic stability, and hydrophobicity. Additionally, hybrids can be formed by including silicates, silanes, and polyfunctional organics which are reactive with the titanate. Titanate oligomers formed by partial hydrolysis of titanate monomer can also be used.

New inorganic binder technology has been developed for thin film zinc rich coating applications. Conventional organic binder approaches have proven to be ineffective in thin film zinc rich application due to their tendency to encapsulate the zinc particles and hence electrically insulate the particles from each other and from the iron substrate. This makes sacrificial activity very difficult to achieve with films that are in the range of 5 to 8 microns. Thin films would be required where threaded parts have tolerance restrictions, and especially where subsequent coatings will be applied over the zinc coating. Conventional inorganic binders based in silicate sol gel technology are also problematic because they tend to post cure (causing topcoat blistering) and are generally very brittle. It can be difficult and costly to modify the rheology and film properties of such binders to achieve desired film properties.

Organotitanates

Organotitanates are suitable as binder materials due to the high reactivity with organic functionality. Titanium can increase its coordination sphere from four to six, enabling stabilization with alcohols as well as reactivity and chelation with functional organics. This high

degree of reactivity also allows the titanates to co-hydrolyze with silanes as well as the surfaces of silica and other mineral pigments. Figure 6 illustrates some possible reactions.

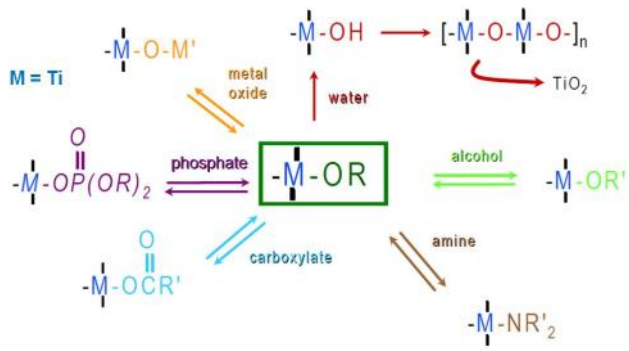


FIGURE 6 – Reactions of Organotitanates

A wide variety of organotitanates were screened, including alkoxy titanates, polytitanates, and chelated titanates. Figure 7 illustrates that the alkoxytitanates are more reactive and provide faster, more complete cure, and are prone to premature reaction with ambient humidity and poor paint stability to gelation. Chelated titanates are much more stable to hydrolysis, but do not provide complete cure at the 400°F bake temperature limit. We found that a blend of an alkoxy titanate and chelated titanate gave the best balance of properties. In addition, a polytitanate was included. This lends some viscosity increase to the binder and improves corrosion performance.

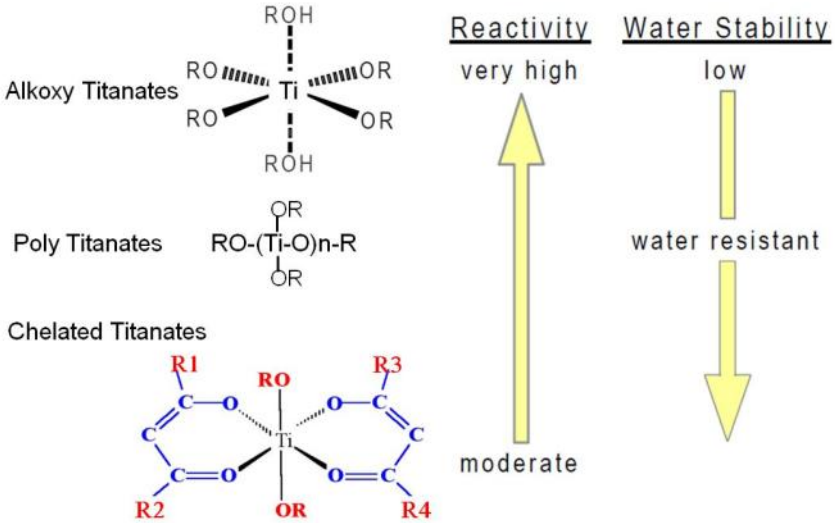


FIGURE 7 - Organotitanate Reactivity vs. Stability

The alkoxy titanate chosen gave the best balance of hydrolysis at elevated temperatures and resistance to moisture at ambient temperatures. We found that a hydrophobic alkoxy moiety surrounding the titanate makes the material hydrophobic enough to remain stable at room temperature far longer than more polar or lower order alkoxy substituents. The titanates can be

further stabilized by the appropriate choice of coordinating alcohol solvent. We found that a blend of low order volatile alcohol such as n-butanol, plus less volatile alcohols with non-polar character such as octanol, gave the best balance of stability and cure.

Stability of the zinc rich primer to premature hydrolysis is a major concern for dip-spin operations. Ambient temperature and humidity conditions in application facilities are often not well controlled. We have shown that high ambient relative humidity greatly reduces the open stir gel time of an alkoxytitanate primer.

Stability of the primer to premature hydrolysis was tested by stirring samples open in the laboratory. The length of the test is dependent upon the ambient humidity conditions. The results in Figure 8 are from testing performed in dry winter months. This shows that the blend which includes chelated titanate lasts approximately twice as long as the alkyl titanate before showing viscosity increase and gelling. Previous test of alkoxy titanate based primers at 30-40 percent relative humidity showed gel times of only 4-10 days. At this writing, we have just begun testing the chelated versions at higher humidity. The results also show the benefit of inclusion in the formula of a molecular sieve to act as a moisture scavenger.

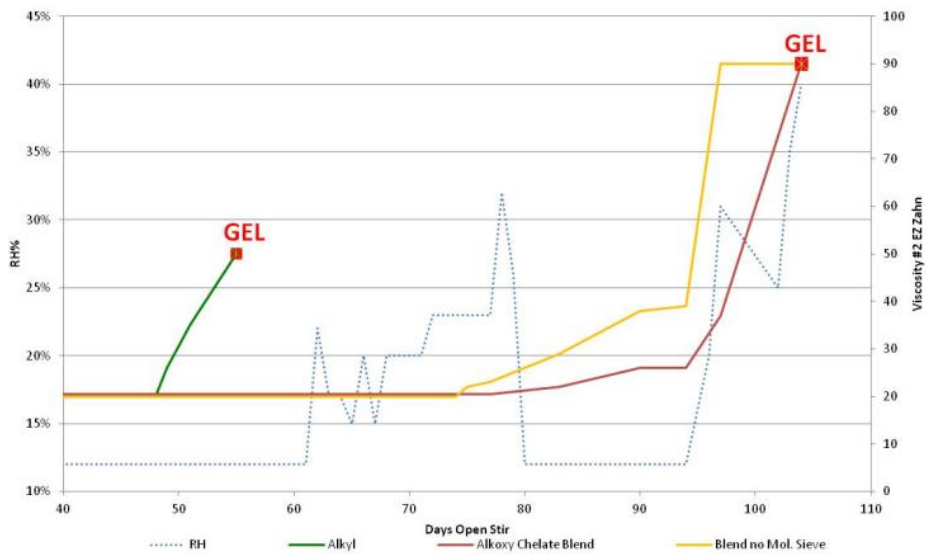


FIGURE 8 – Open Stir Stability Test

Organic/Inorganic Hybrids

Binders tested in this work included titanate-silane hybrids, with, and without modification with an organic diol. It was found that the addition of organic diol will decrease the film shrinkage and brittleness. Figure 9 shows SEM images of films cast from the binders with increasing organic diol concentration. It is clear that a more continuous film results from lower shrinkage.

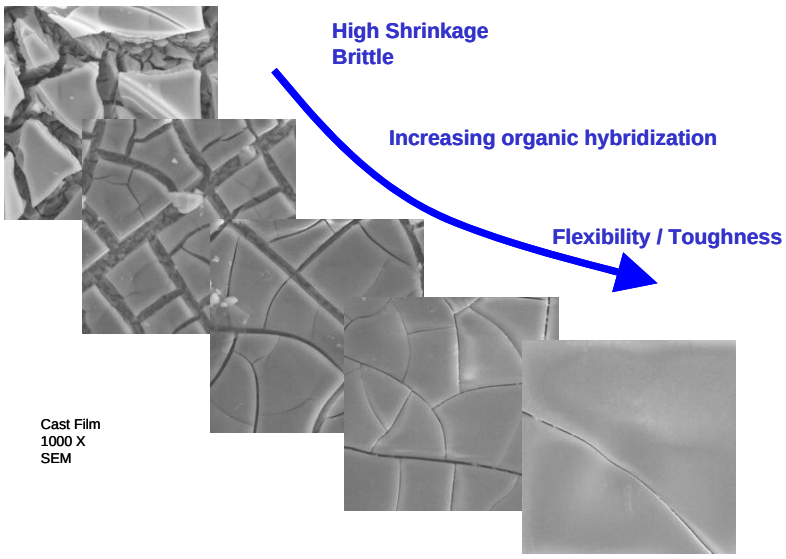


FIGURE 9 – Effect of Organic Hybridization on Inorganic Titanate binder

When a zinc rich flake primer is formulated with these inorganic-organic binders, there is a significant effect of organic on corrosion performance. Inclusion of an organic polyol, and the resultant shrinkage decrease, allows the binder to encapsulate the zinc flakes to a greater extent. As was seen with the all-organic binders, this partially insulates the flakes. If the organic content is not too high, the corrosion rate of exposed zinc is slowed, while still maintaining some sacrificial activity (Figure 10).

No Organic Organic Modification

FIGURE 10 – 1000 Hours B117 Salt Spray Comparison

Hybrids were also formed using bis-phenol A based epoxy resins. It was hoped that this would improve the barrier and corrosion properties. However, we found that the epoxy also coated the Zinc and reduced sacrificial performance. Many other functional organics were screened with similar results.

In addition to slowing the rate of corrosion of the zinc, we have found that organic modification can also affect the morphology of the zinc corrosion products. Figure 11 shows that a pure zinc (hot dip galvanized panel) surface corrodes very rapidly in salt spray exposure. The resultant zinc corrosion products (oxide, hydroxide, and carbonate) are very amorphous and not adherent. This allows more zinc to be exposed and thus the zinc is rapidly consumed. The zinc which is partially encapsulated in the hybrid binder shows zinc corrosion products which are very tight crystalline structure. This well formed crystal morphology acts to seal the surface

from further corrosion and acts as a barrier. We theorize that the ratio of components of the corrosion products is different; however, this has not been proven by analysis.

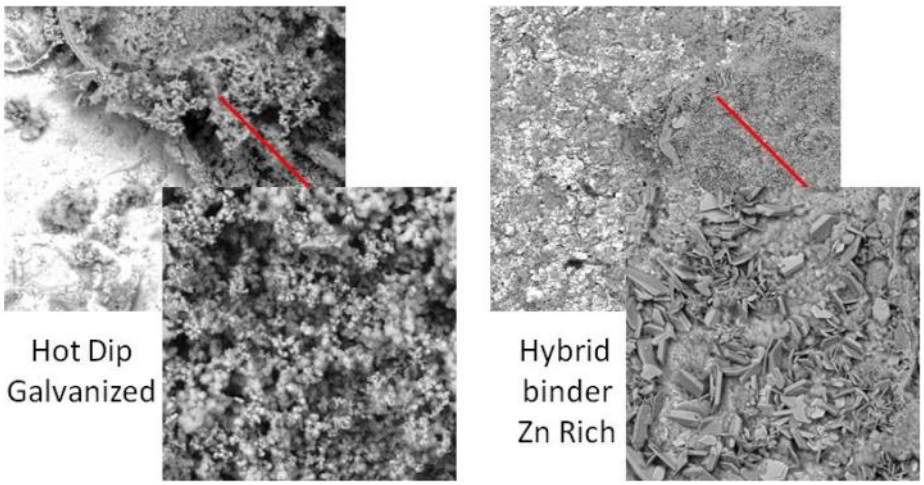


FIGURE 11 – Zinc Corrosion Products (Salt Spray)

For applications where the zinc rich primer must stand alone without topcoat, the organic modification is necessary to form a continuous binder phase and an adequate barrier film. However, we have shown that for topcoated zinc rich applications such as fasteners, the corrosion mechanism is changed, and mitigation of the zinc corrosion rate by encapsulation is detrimental. This effect is discussed in more detail in a later section of this report.

We have also found that organotitanates can readily co-hydrolyze with organosilanes. We have included an organosilane in the binder formula which improved wetting of the zinc flake surface and promotes cohesive strength within the zinc primer. This material also helps wet the surface of, and bond to other silica based pigments included in the formulation for rheology control and anti-settling. We also were able to form hybrids with silanol functional polysiloxanes. However, these showed the same insulating behavior as the organic hybrids; leading to poor corrosion performance.

Zinc Rich Primer – Zinc Flake Development

There are currently several commercial sources offering zinc flakes. These are traditionally produced by flattening zinc dust, typically in a ball mill. This process is done in both dry and wet milling processes. The main drawback of these conventional materials is that they must use lubricants such as stearic acid or fluorocarbons which can cause poor cohesion within the zinc primer as well as poor adhesion of subsequent topcoats.

The current work investigates flakes made by a processes in which conventional lubricants are minimized and which produces a particle size and shape distribution which is compatible with the topcoat and gives improved performance. Further, the flake is dark in color which minimizes bright spots showing through the topcoat at “touch points” where the fasteners contact each other during processing. This is especially objectionable where black topcoat is used.

We have found that sacrificial corrosion performance in thin film zinc rich coatings is greatly enhanced by the use of flakey zinc particles versus spherical zinc dust particles. The effect can be seen in Figure 12 where after 24hrs of salt-spray exposure, the coating containing spherical zinc dust particles shows the formation of red rust. Conversely, the coating produced with the same concentration of zinc flakes shows no evidence of red corrosion of the steel substrate.

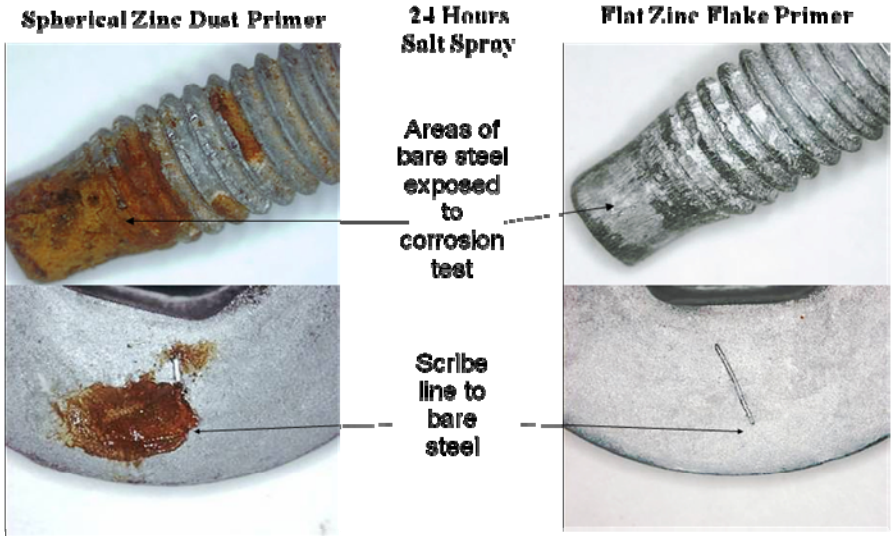


FIGURE 12 – Sacrificial Corrosion of Zinc Dust versus Flakes

This is presumably due to the fact that the flake particles are capable of overlapping to give high surface area contact between zinc particles and the substrate (Figure 13). It is very difficult to achieve this type of electrical continuity with a spherical zinc dust film since the area of contact between spheres is very small.

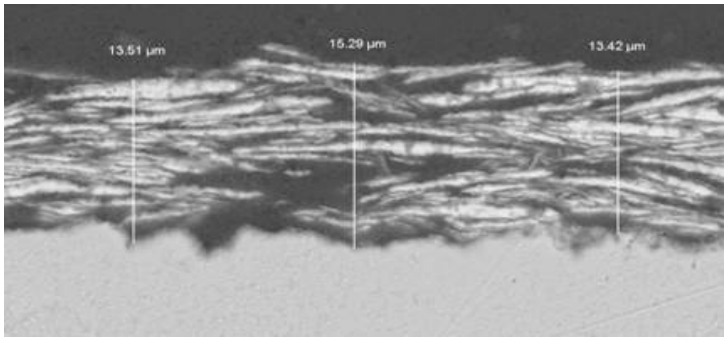


FIGURE 13 – Cross-section of a Zinc Flake Coating

Several commercially available zinc flake materials were screened. In all cases, when formulated with the inorganic binder discussed above, the resultant primer films exhibited poor adhesion to electrodeposition topcoat (PPG Powercron XP). All of these materials were described as “flaking” grade and were presumed to have significant levels of stearic acid included as a lubricant. In addition, these materials were very costly in comparison to the zinc powder from which they are made.

Much of the early work in this project involved development and optimization of a wet milling process to produce zinc flake from fine grade, low lead zinc powder. The goal was to be able to blend the primer ingredients and mill in conventional milling equipment to produce a flake. This would minimize raw material costs and allow us to control flake size and shape.

Early attempts revealed a significant challenge. There are ingredients, including solvents, which contain hydrogen. We found that milling zinc in the presence of these materials caused rapid generation of hydrogen gas. In many cases, the slurry would rapidly entrain the gas and turn to the consistency of soft ice cream. Other batches would remain fluid during milling, but generate hydrogen and build pressure in the container. This created an unstable and dangerous situation.

We were able, however, to identify a particular type of milling equipment in which the energy input could be carefully controlled. There is a narrow window in which enough mechanical energy is provided to flatten the powder to flake, but not cause the adverse hydrogen generating reactions. Many formulation parameters as well as milling parameters were found to be critical to success without gassing. It is important to note that the formulation does not include high levels of lubricating materials such as stearic acid which can adversely affect topcoat adhesion. Instead we are taking advantage of lubricity provided by the binder and solvents.

In addition to achieving flake without gassing, we were able to carefully control the process duration such that the spherical powder was flattened enough to provide lamellar overlap, but not to the extent where the resultant film would be to smooth and non-porous as was seen with commercially available flakes (Figure 14). This resulting porosity allows the topcoat to penetrate and tenaciously adhere to the zinc flake matrix.

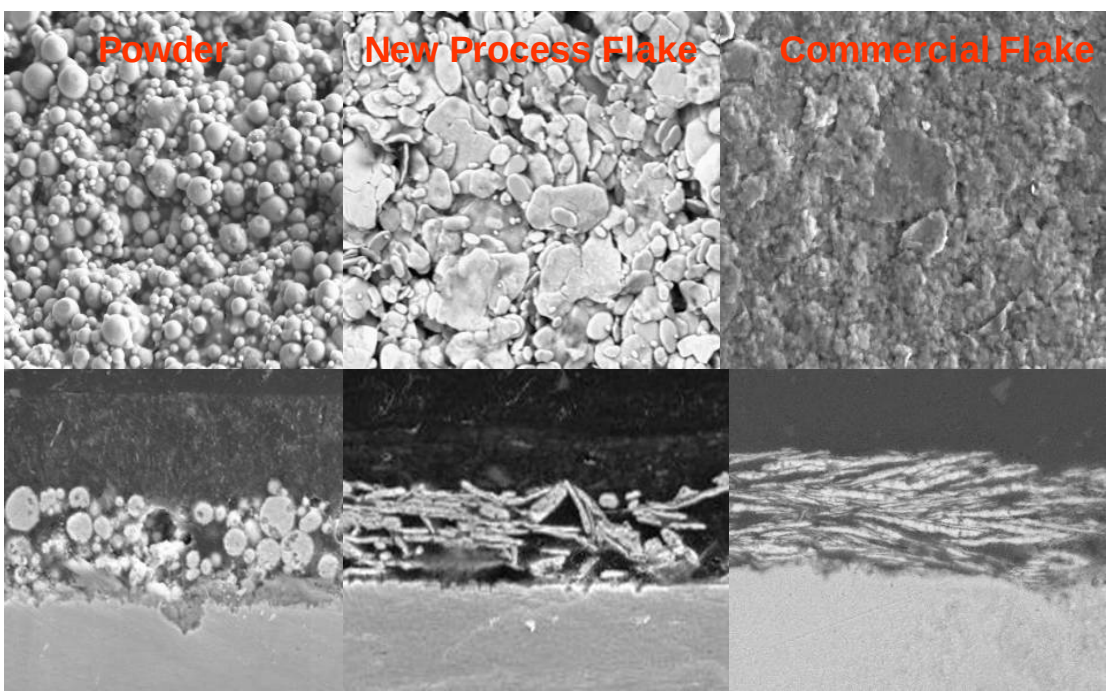


FIGURE 14 – SEM Photos of Zinc Powder and Zinc Flakes.
Top View and Cross Section (below)

Although we were able to optimize this process and made several production size batches, it was evident that the process is very difficult to monitor. Large scale production with batch-to-batch reproducibility would be difficult. A different process involves conversion of the powder in a dry milling process using low levels of lubricants. Additionally, the flake can be made dark in color. This is very desirable so that "touch" marks and other damage spots on a fastener do not appear bright silver through the topcoat.

Work was done to optimize this dry process and successful production scale material has been made. The material gives excellent adhesion characteristics and corrosion performance.

Other Flake Work

Mixed Metals – Testing was done to determine the effect on corrosion performance by the addition of minor levels of aluminum or tin with the zinc. Both were added as alloys and as powders in the milling process. Aluminum was also tested as flake blended with zinc flake.

Blending of aluminum flake with the zinc flake gave the greatest benefit in corrosion performance. Aluminum flake was added to commercially available zinc flake at a level of 20 percent of the metal content. Several aluminum flake grades were tested with similar results. It appears that the addition of the aluminum acts to improve the barrier properties of the primer and may also mitigate the corrosion rate of the zinc[11]. The result was most pronounced where no topcoat was present. There was much less white rusting on panel surfaces. The effect was similar to the addition of organics to the binder.

Performance with epoxy electrodeposition topcoat was also improved over flat panels, however, more red rust spots were evident on fasteners at 1000 hours B117 Salt Spray. The addition of aluminum seemed to electrically "cool" the cured film, resulting in a more defect-free electrocoat application. This gives fewer white rust spots. It appears that the slower zinc corrosion rate is a detriment for topcoated application. All variants gave unacceptable topcoat adhesion.

Some work has been done with blending aluminum flake with the new dry milled flake, however, topcoat adhesion becomes unacceptable at relatively low levels of aluminum. There was also a greater frequency of small red rust events on fasteners at >1000 hours B117 Salt Spray. Work continues in this area.

Similar improvements to flake blends can be achieved by blending aluminum (or tin) powder with zinc powder and co-milling to form flake. This was tested in the wet milling process and has not yet been applied to the preferred dry process.

Flakes made from zinc/aluminum and zinc/tin alloys were also tested. These were commercially available materials. Although both gave improved barrier performance and slower zinc corrosion rate, both gave unacceptably poor topcoat adhesion with epoxy electrocoat. Also, these materials are prohibitively costly for this application.

Flake surface abrasion – During development of the wet milling process, materials were included in the grinding stage in efforts to abrade the flake surface. The intent was to improve adhesion/cohesion characteristics by roughening the flake surface. Figure 15 shows clearly that the inclusion of silicon/aluminum oxide or aluminum oxide will cause rougher surface topography. However, corrosion and adhesion testing of these materials did not reveal any

advantage. Inclusion of fumed silica in the grind did improve adhesion, however, the same level of silica added separately after milling gave the same improvement. This abrasion approach has not yet been applied to the dry process.

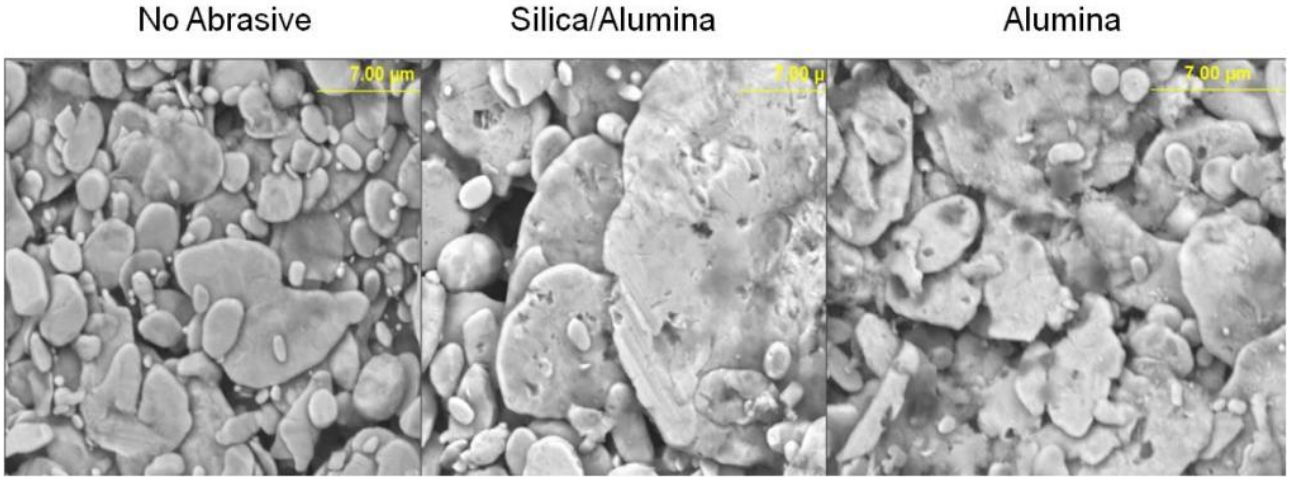


FIGURE 15 – Surface Abrasion of Zinc Flake

Zinc Rich Primer – Optimized Formulation

Formulation **-** The optimized zinc rich primer formulation includes the binder and dry process flake described above. The loading of metallic zinc is approximately 90 percent. In addition, a solvent blend has been chosen for optimal stability, flow, and polarity. This includes both active solvents such as butanol and inactive solvents such as aromatic type 100 (e.g. Solvesso 100, Exxon). The active solvents not only stabilize the titanate, but interact with other ingredients in the formula. These include minor components such as bentonite clay, surface treated silica, molecular sieve silica, and polymeric thixotropic agents. These materials are added to control hard settling of the zinc as well as wet flow (sag) control. Since the inorganic binder has little viscosity or "body", these additives are necessary to control the ability of the wet coating to evenly cover a complex shape such as a threaded fastener. The molecular sieve silica is included to scavenge moisture which may be brought by other components.

Application – The primary intended application method of the zinc rich primer is by conventional dip-spin process. This involves loading parts into a basket and submersing it into a vat of paint. The basket is then raised above the paint surface and spun to remove the excess liquid by centrifugal action. The parts are then emptied onto a conveyor belt which passes through a curing oven. For this development, a small spin basket was mounted to an electric motor with digital speed control (Fig 16). Lab sample were spun at 350-500 rpm for 20 seconds.

This material can also be applied by dip-drain, or spray. It is not recommended for brush or roll application. Lab test panels were prepared with a wirewound drawdown bar.

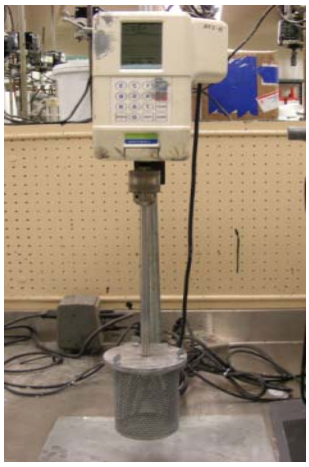


FIGURE 16 – Lab Dip-Spin Apparatus

Table 1 and Figure 17 list typical physical properties and bake curing requirements.

Typical Properties –

SOLIDS % BY WEIGHT (@400°F)	65% ± 1.0 %
SOLIDS % BY VOLUME (@400°F)	22% ± 1.0 %
WEIGHT/GALLON:	15.5 lbs/gal ± 1.0
COVERAGE	500 sq. ft. per gallon per mil at 100% efficiency
60° GLOSS:	0 - 10
COLOR:	Gray
PACKAGE VISCOSITY@77°F:	25-40 Sec. #2 EZ Zahn
APPLICATION VISCOSITY	18-30 Sec. #2 EZ Zahn (dip-spin)
REDUCTION	Aromatic 100, Aromatic 150, Butyl Cellosolve
V.O.C:	5.5 lbs./gallon
SHELF LIFE:	6 months (closed container)
FLASHPOINT (PENSKY-MARTENS):	118°F / 48°C
CURE	400-600°F (204-315°C) / 15 minutes @ metal temp
OVEN TYPE	Indirect Gas or Electric
FLASH TIME	0-10 minutes

TABLE 1 – Zinc Rich Primer Physical Properties

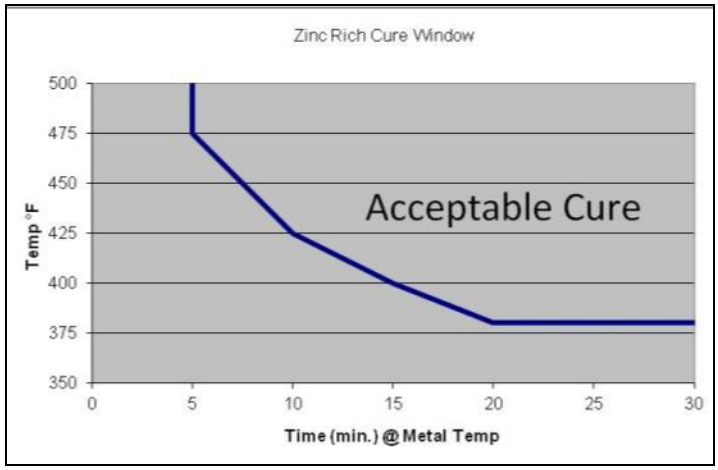


FIGURE 17 – Thermal Cure Window

Topcoat Formulation

<u>Electrodeposition Topcoat</u> – We did not attempt to reformulate the basic composition of the cationic epoxy electrocoat. This material is currently in commercial use at fastener applicators in North America as Powercron XP (black). It meets requirements of automotive, industrial, and construction fastener manufacturers. It has broad specification approval as a fastener coating.

However, DoD end users have expressed the a desire for a range of topcoat colors, other than the standard black desired by automotive customers. It is felt that color coding of different

fastener types may be necessary. It is possible to formulate the pigmentation of this coating to meet most any color requirement. To demonstrate this, we made a gray and a green version. Figure 18 shows the appearance and demonstrated that salt spray performance is equal.

FIGURE 18 – Ecoat Topcoat Color Variations

It is possible to match the color for specific applications. In addition, it is possible to adjust this formulation to meet specific torque / tension requirements. It should be noted that specialized electrocoat formulations may require new electrocoat application installations if part volumes are substantial. In cases where the volume of parts will be relatively small, the application equipment could easily be structured for swapping of multiple colors and/or torque formulations. The application equipment can be tailored to any size; continuous or batch process. It is conceivable, for instance, that a repair depot or shipyard could have electrocoat application on site.

Although all of this work has been done with cationic epoxy electrocoat, there are also approved cationic acrylic electrocoat materials with broad fastener specification approvals. This could be used in applications where UV durability is required.

Aluminum Rich Topcoat – A significant amount of work has been done to develop a new aluminum rich, solvent based topcoat for use over the zinc rich primer. This is necessary to make the zinc rich technology available for use at application sites where electrodeposition is not in use. This would be a liquid topcoat which would be applied by conventional dip-spin methods. The key requirements are the same as for the electrocoat topcoat in that it must provide adequate barrier performance for a minimum 1000 hours salt spray, and also provide torque/tension characteristics.

It has proven to be a significant challenge to achieve uniform coverage without thread fill for an organic binder based topcoat. Unlike the inorganic binder used in the zinc rich primer, the thermoset epoxy resin used in this formula has much different rheology and less shrinkage. Obtaining a uniform thin film without thread fill was achieved through careful balance of resin

molecular weight, solvent choice, application solids, and application viscosity. In addition, the dip-spin application conditions proved to be critical. Figure 19 shows the appearance and thread fill characteristics of the best candidate formulation on various fasteners.

FIGURE 19 – Aluminum Rich Topcoat Appearance and Thread Performance

The best optimized formula at this writing gives even silver/gray appearance, meets torque/tension requirements, and passes 1000+ hours salt spray performance. We have found, however, that this is less uniform and not as good a barrier as the electrocoat topcoat when applied in a single coat over zinc rich primer. Adequate coverage is achieved to prevent red rusting with only sporadic red spots at 1000 hours salt spray, but there is significant white corrosion and "tarnish" evident. Substantially improved corrosion performance can be achieved by applying two consecutive thin coats of the aluminum rich topcoat (see test results, example 4). This is the preferred system. Typical properties are listed in Table 2.

SOLIDS % BY WEIGHT	55% ± 1.0 %
SOLIDS % BY VOLUME	40% ± 2.0 %
WEIGHT/GALLON:	8.7 lbs/gal ± 1.0
COVERAGE	800 sq. ft. per gallon per mil at 100% efficiency
60° GLOSS:	NA
COLOR:	Silver / Gray
PACKAGE VISCOSITY@75°F:	25-30 Sec. #2 EZ Zahn
APPLICATION VISCOSITY@75°F:	18-25 Sec. #2 EZ Zahn (dip-spin)
REDUCTION	Aromatic 100, Aromatic 150, Dow PM Acetate
V.O.C:	4.5 lbs./gallon
SHELF LIFE:	6 months (closed container)
FLASHPOINT (PENSKY-MARTEN):	103°F / 39°C
CURE	375-400°F (191-204°C) / 15 minutes @ metal temp
OVEN TYPE	Indirect Gas or Electric
FLASH TIME	0-10 minutes

TABLE 2 – Aluminum Rich Topcoat Physical Properties

Corrosion Mechanism Considerations

As discussed earlier, we have found that there is a significant difference in corrosion performance between topcoated and un-topcoated zinc rich primer. Formula variations which tend to improve bare or "stand-alone" zinc rich performance generally will degrade topcoated performance. Factors which mitigate the zinc corrosion rate, insulate the zinc flake, or decrease the electrical conductivity of the primer, will decrease the "healing" capability of the topcoated paint system. These include organic modified binders and addition of aluminum flake. Figure 20 shows this effect on fasteners after 1000 hours salt spray exposure.

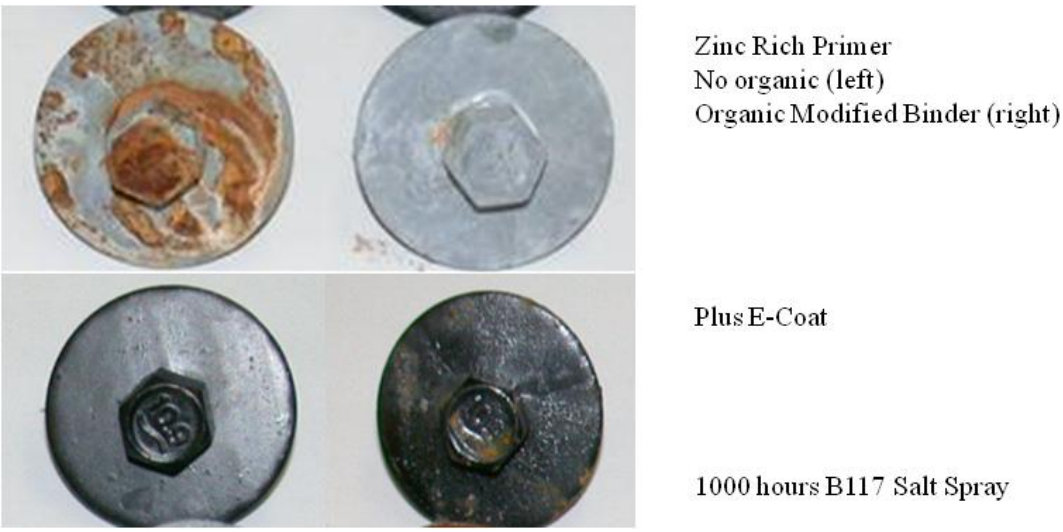


FIGURE 20 – Effect of Topcoat Over Zinc Rich on Corrosion

Our work leads to the conclusion that the corrosion / protection mechanism and function of the zinc rich primer is different when topcoated. In the case where no topcoat is present, the entire zinc surface is exposed to the electrolyte environment and is available to act as a sacrificial anode to protect the iron substrate. This is akin to galvanizing. In this situation, the zinc layer must have good barrier properties and the zinc must be protected from rapid degradation. If the zinc corrodes too fast and the corrosion products are loose and amorphous, there will be depletion of the zinc and red rust will occur.

Conversely, when a zinc rich primer is topcoated, the topcoat acts as a barrier and insulates the bulk of the zinc from the electrolyte. In this case, the bulk of the surface is protected by the topcoat barrier properties and the zinc acts in small areas of damage such as "touch points", part-to-part collision damage, and topcoat defects such as pinholes. For fasteners, these are small, localized corrosion events. Therefore, the only zinc that is available to act as a sacrificial anode is the zinc exposed in the damage area where topcoat is penetrated (Figure 21). If this zinc surface area is too small with respect to the exposed steel, a red rust spot occurs. If the zinc at that local damage spot does not have adequate electrical contact with the steel, then there is no sacrificial action and red rust occurs.

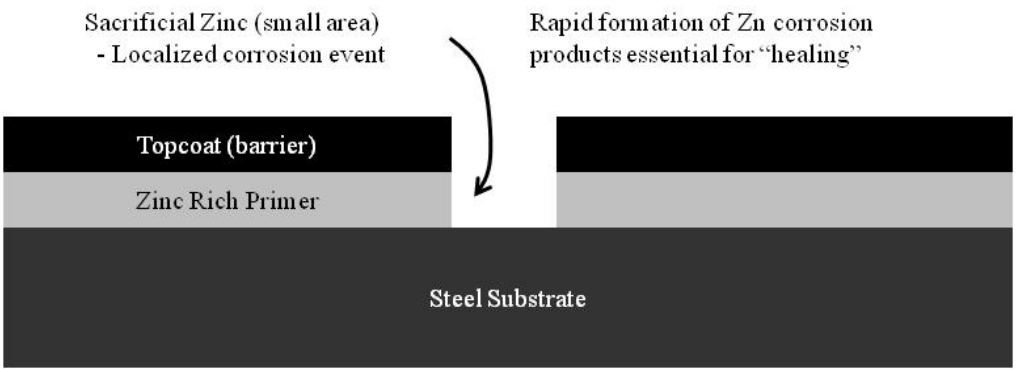


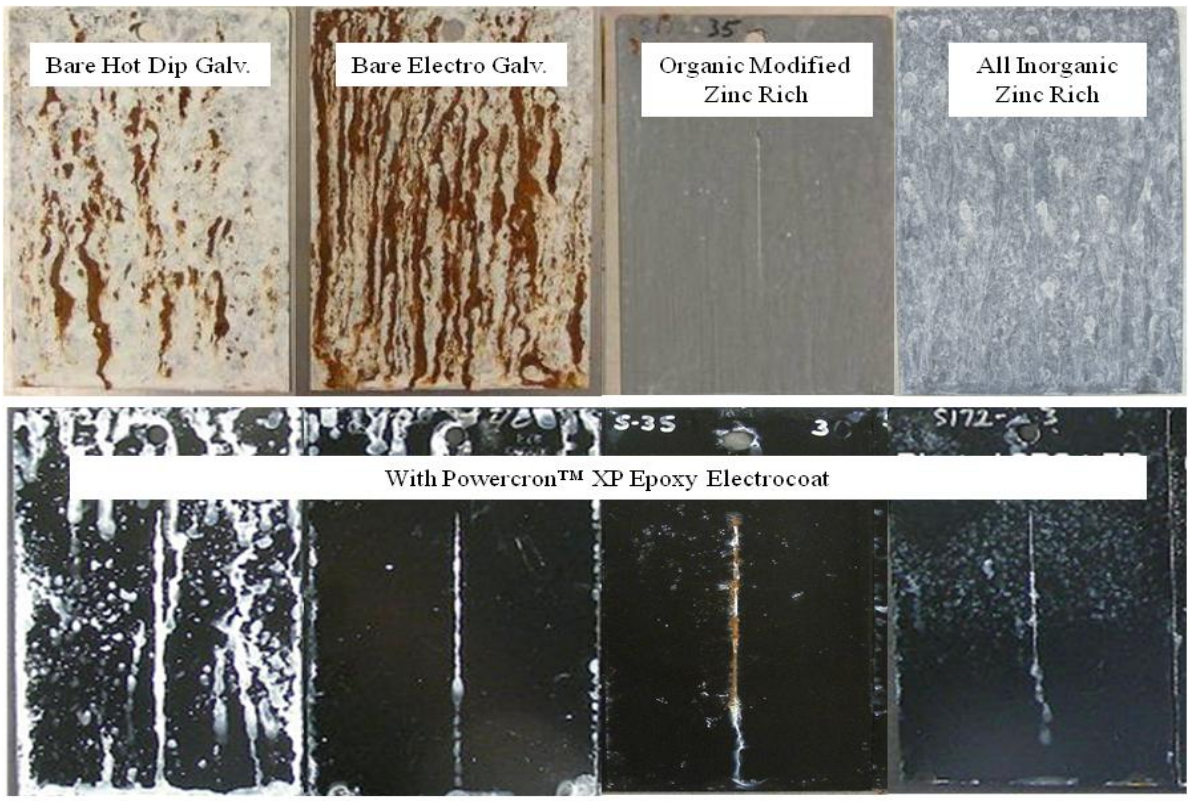
FIGURE 21 – Localized Corrosion Event Schematic

In addition to the sacrificial activity of the Zn/Fe couple, corrosion in local spots is accomplished through a "healing" mechanism. If the exposed zinc can form corrosion products rapidly, AND those corrosion products form a tightly bonded crystal structure, they will seal the defect and prevent further corrosion. In addition, these corrosion products can act as alkaline anticorrosive agents. In fact, it may be true that this "healing" effect is the dominant corrosion control mechanism in topcoated, thin film zinc rich applications such as fasteners.

Corrosion protection in this situation is especially difficult in fastener applications since the zinc rich (and topcoat) must be relatively thin in film thickness to comply with thread mating requirements.

Figure 22 shows a comparison of organic modified and unmodified zinc rich primer with hot dip (HDG G70 70U, ACT Laboratories, Inc.) and electroplated galvanized (E60 EZG 60G, ACT Laboratories, Inc.) panels. It is clear that the rapid corrosion of zinc helps "heal" the damaged areas (scribe and pinhole defects).

It is important to note that the salt spray environment is extremely aggressive toward bare zinc surfaces. Hot dipped galvanized parts such as fence posts have endured outdoor exposure, even in coastal environments, for many years. There is wide consensus that salt spray is inappropriate for predicting real world performance of zinc substrates. However, it is still almost universally used as a performance requirement in specifications for zinc rich coatings and fasteners.



500 Hours B117 Salt Spray

FIGURE 22 – Comparison with Galvanized Corrosion

Test Results

<u>Material Descriptions / Definitions</u>

Test Fasteners -	Various automotive fasteners (various sources) M10 Grade 8 (Fastenal Co.) M10 Grade 10.9 test bolts(Wilson-Gardner Co. #345 HHM10150060-10S) Torque/Tension spec. test bolts (GM, Ford, Chrysler (W.G. Co.)
Zinc Phosphate 1 - (C700)	Chemfos C700C59 (abbreviated C700) Fine crystal zinc phosphate with non-chrome rinse Flat panels from Advanced Coatings Technology (ACT) Fastener parts processed by PPG Industries, Inc.
Zinc Phosphate 2 - (Z24)	Irco Bond Z24 (abbreviated Z24) Medium/large crystal zinc phosphate with non-chrome rinse Panels and parts processed by PPG Industries, Inc.
Cadmium Plating - (Cd/Cr)	Per QQ-P-416 Type II, Class 2 Cadmium yellow with Chromium +6 rinse Embrittlement relief bake 375°F±25 for 23 hours (within 4 hrs.)

	Processed by DeTray Plating Works (Independence, Mo.)
Zinc Rich Silver -	Early experimental candidate made by wet mill process
	Light in color, weak for cohesion/adhesion
	Typical film thickness 6-8 microns (µ)
	Applied by dip-spin method
	Bake cured at 400° for 20 minutes
Zinc Rich Charcoal -	Latest zinc rich primer candidate at this writing
(optimized formula)	Optimized formula made with dry flake process
	Application and cure same as silver above
Aluminum Rich -	Experimental organic aluminum rich topcoat candidate
	Applied by dip-spin method over zinc rich primer
	Typical film thickness 6-10µ
Electrodeposition Topcoat -	Cationic epoxy applied by conventional electrodeposition method
(E-Coat, Ecoat)	All parts coated in PPG laboratory (except production trials)
	Powercron XP (black, gray, green) (PPG Industries, Inc.)
	120-220 volts / 90°F / 90 seconds – Bake 375°F / 20 minutes
	Target film 8-10µ over zinc primer / 15-18µ over steel
Hydrogen Embrittlement -	ASTM F519-06e2 Type 1a.1, AISI E4340 notched bars.
	Fabricated and certified by EXOVA (Santa Fe Springs, CA)

Salt Spray (ASTM B117) **–** Note: These examples represent the best performance achieved with these coating systems. Corrosion performance can vary depending upon the quality of the substrate, the number of "touch point" defects, and the consistency of the film thickness of the coating layers.

Example 1- Zinc Rich plus Electrocoat – Grade 10.9, Size M10 x 2.5” Hex Bolts. Alkaline cleaned and treated with zinc phosphate Z24. Cationic black epoxy E-Coat, plus Cadmium controls. Figure 23 shows exposure results of sets of 10 industrial grade bolts. A pinpoint of red rust is circled in red. The samples with zinc rich primer are superior to electrodeposition alone, but not as strong as cadmium.

Electrocoat (~15µ) over zinc phosphate
1000 Hours
Red rust on all samples appears at approximately 250 hours.

Zinc rich primer (~6µ) over zinc phosphate plus electrocoat (~8µ)
2000 Hours
1 small red spot

Zinc rich primer (~6µ) over zinc phosphate plus aluminum rich topcoat (~6µ one coat))
2000 Hours
No red rust spots

Cadmium low Cr rinse
2000 Hours
No corrosion evident

FIGURE 23 – Salt Spray Corrosion Results

Example 2 – Automotive grade 9.8 M10 bolts with zinc phosphate Z24, zinc rich charcoal formulation, and black E-Coat . Figure 24 shows significant white rusting and only a few small red rust spots after 3000 hours on sets of 8 automotive grade bolts. Pinpoint red rust spots are circled in red.

FIGURE 24 – 3000 Hours Salt Spray Exposure

Example 3 – Flat panels, cold rolled steel, zinc phosphate C700, zinc rich charcoal primer and black E-coat or aluminum rich topcoat (single coat). 1000 hours exposure. Cadmium is included for reference. Figure 25 shows strong performance of the zinc rich primer, with no red rust, but not as strong as cadmium.

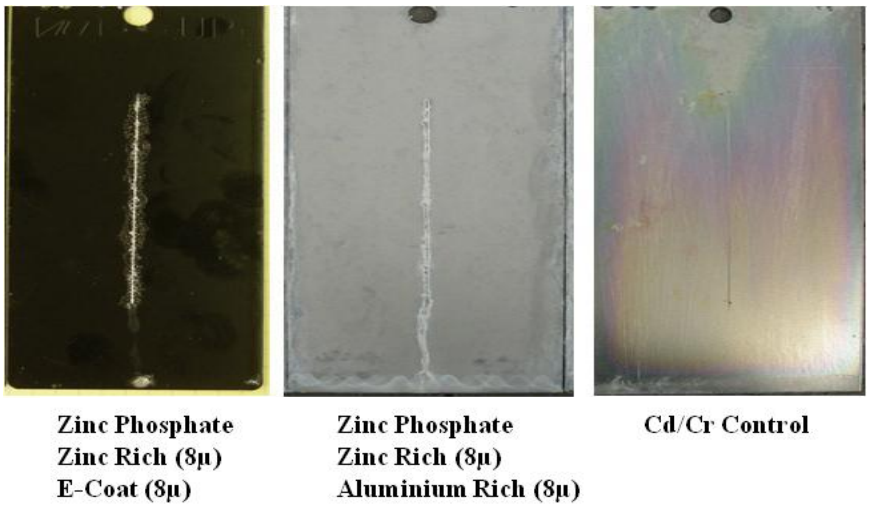


FIGURE 25 – 1000 Hours Salt Spray – Flat Panels

Example 4 – Aluminum rich topcoat; single versus double coat; 1000 hours exposure versus electrocoat. Figure 26 shows clearly that the two coat application provides far superior barrier protection. The single coat allows more zinc exposure and can only be applied at 6µ maximum without poor thread fill properties. Attempts to apply a single coat at 8µ lead to unacceptable thread gapping stuck washers. However, it is possible at lower viscosity and higher spin speed to achieve very even coats of 5-6µ. Multiple applications also greatly reduces the possibility of touch points to bare zinc primer.

Zinc Phosphate Zinc Rich (8µ) Electrocoat(8µ)	Zinc Phosphate Zinc Rich (8µ) Aluminium Rich (6µ) (single coat)	Zinc Phosphate Zinc Rich (8µ) Aluminium Rich (8µ) (two coats @ 4µ ea.)

FIGURE 26 – Aluminum Rich Single vs. Double Coat Salt Spray, 1000 Hrs

<u>Cyclic Corrosion</u> – GM9540P (General Motors Corp.)

Grade 8 M10 (left), Grade 10.9 M10 (right). zinc phosphate Z24,zinc rich charcoal primer, black E-Coat. No red corrosion. Note: Cadmium controls were not included but expected to perform very well. Figure 27 shows only white corrosion on sets of five industrial grade fasteners.

FIGURE 27 – GM9540P – 100 Cycles – No Red Corrosion

SO_2 Acidified Salt Spray – ASTM G85

Grade 10.9, Size M10, zinc phosphate Z24, charcoal zinc rich primer (7µ), black E-Coat (9µ); versus cadmium control. Figure 28 shows sets of five industrial grade bolts. Cadmium controls are badly red rusted after only 288 hours, while the zinc rich plus electrodeposition coated parts have only a few pinpoints of red rust and moderate blistering.

FIGURE 28 – ASTM G85 SO_2 Salt Spray

Adhesion / Cohesion – ASTM D3359

We have found that adhesion of electrocoat and aluminum rich topcoats to the zinc rich primer has been consistently excellent throughout this development effort; with the exception of primers made with commercially available zinc flakes. We have also seen very good adhesion of zinc primer to the zinc phosphate and bare steel substrates for most formulations. In most cases where failure of the crosshatch is seen, the failure mode is cohesive within the zinc rich primer layer. This is evidenced by the presence of zinc primer on the tape and on the metal substrate.

The most critical factor influencing cohesive failure is the film thickness of the zinc rich primer. While early formulations were adequate in the 4-7µ range, they showed poor cohesion and significant loss above this range. Higher film build cohesion is necessary not only to protect areas of fasteners where the film may be high, but also for dip-drain and spray applications where thicker films are desirable.

For comparison purposes, we compare here early silver color zinc rich formula candidate made with the wet milled process, to the newer, optimized charcoal formula made with dry milled flake. Figure 29 shows the tape adhesion improvement on flat panels with E-Coat over zinc rich primer at various film thicknesses. The e-coat was applied at approximately 10µ. It is clear that the reformulated binder and dry flake combination give much improved cohesive strength within the primer.

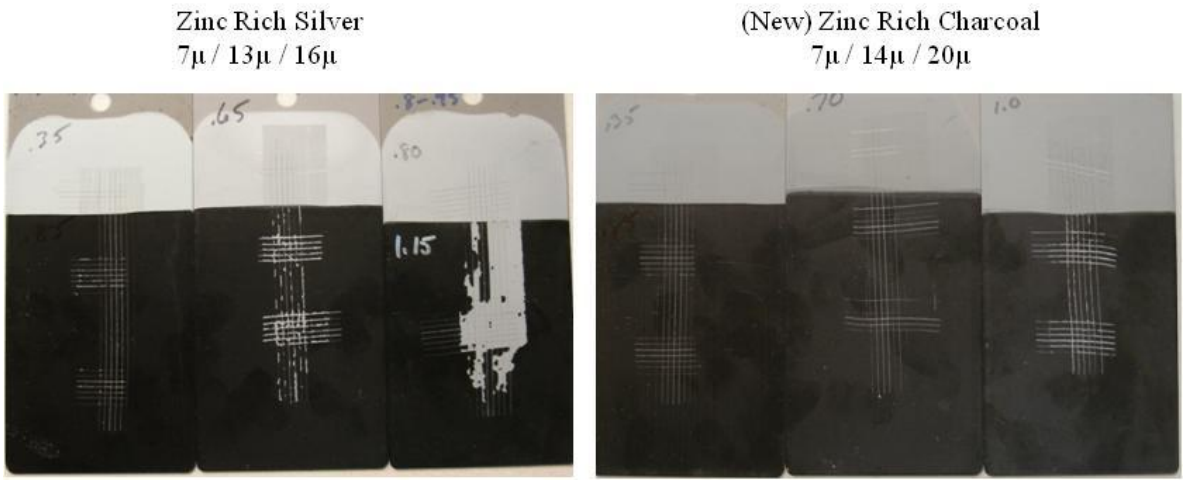


FIGURE 29 – Adhesion / Cohesion versus Primer Film Thickness

Figure 30 illustrates improved adhesion over bolts which have been vigorously shaken in a container for one minute. This is far more severe than the damage that would be seen in a production environment. Again, the optimized primer shows less damage and the touch points are less visible.

FIGURE 30 – Bolt Shake Test

Thread / Recess Fill – The zinc rich primer, electrocoat and aluminum rich topcoats all give excellent evenness of coverage on threads and in recessed head areas. For all bulk coated parts, however, there is always a tendency for flaws where large areas of contact between parts and racking surfaces occur. Figure 31 illustrates the lack of thread or recessed head fill by the zinc rich primer, electrodeposition topcoat, or the aluminum rich topcoat.

FIGURE 31 – Thread and Recess Fill - Left to Right, zinc rich M10, (zinc rich plus E-coat M10, M6, M6, M4), Zinc rich plus Aluminum rich topcoat (2 coats) M10, Zinc rich M10 recessed head.

Hydrogen Embrittlement - ASTM E8-88, ASTM F519 1a.1.

Conventional electroplating processes such as those employed for cadmium plating of fasteners are known to cause hydrogen embrittlement of high strength steel alloys[5]. These processes trap hydrogen gas within the grain structure of the steel alloy. This gas can cause structural weakening of the steel and catastrophic failure of a fastener.

Concerns have been raised about the potential for hydrogen embrittlement due to electrochemical actions which occur during application of an electrodeposition coating system. This is of particular concern for high strength fasteners.

Since the electrodeposition layer is applied only over the zinc and not the bare steel, it would not be expected that hydrogen penetration would be possible. Even in cases where electrodeposition is carried out directly over the steel (with phosphate conversion coating), it is believed that hydrogen embrittlement will not occur. To verify this, a study was conducted to quantify any effects on the strength of steel components due to hydrogen generation during the electrocoat process.

To measure any embrittlement, the test study used ASTM E8-88 for Tension Testing of Metallic Materials. Several parts were tested before and after electrocoating for hardness (Rockwell B), 0.2% Yield Strength and Ultimate Tensile Strength. From the data summarized in Table 3, no significant changes were observed in the strength of the part after the cathodic electrocoat process. This testing was done strictly to test embrittlement of steel with electrocoat application (no zinc rich primer).

Test	Not Electrocoated	Electrocoated
Spec Diameter (inches)	0.252	0.252
Area (square inches)	0.049	0.049
Hardness - Rockwell B	80.0	86.0
0.2% Yield Strength (psi)	144300	142900
Ultimate Tensile Strength (psi)	152500	151300
% Elongation over 1 inch	19.0%	17.5%
% R&D Area	61.2%	59.1%

TABLE 3 - Cathodic Electrodeposition ASTM E8-88 Performance Results

Testing was also done to confirm that the full coating system including zinc rich primer plus electrodeposition topcoat does not cause hydrogen embrittlement. There is also concern that embrittlement can occur due to hydrogen generated by the electrochemical reactions involved in the sacrificial cathodic action of the Zn-Fe couple. Hydrogen can also be generated during rapid oxidation of the zinc layer[6]. This is often called in-service embrittlement or re-embrittlement.

The first test set included several variables including surface preparation; sand blast versus zinc phosphate C700, and topcoats; gray electrocoat (Powercron XP) versus aluminum rich topcoat. All received zinc rich primer (early silver version) by dip-spin. In addition a duplicate set was exposed to 1000 hours of ASTM B117 salt spray before tension testing. This was done to show the effect of sacrificial electrochemical activity and in-service embrittlement. Unexposed bars were stored in a desiccator and all were tension tested at the same time. Results are listed in Figure 32.

Sample (x4)	Prep	Topcoat	Salt Spray	Result
A	Zn Phosphate	E-Coat	none	PASS
B	Zn Phosphate	Al Rich	none	PASS
C	Grit Blast	E-Coat	none	PASS
D	Grit Blast	Al Rich	none	PASS
E	Zn Phosphate	E-Coat	1000 Hrs	FAIL
F	Zn Phosphate	Al Rich	1000 Hrs	FAIL
G	Grit Blast	E-Coat	1000 Hrs	FAIL
H	Grit Blast	Al Rich	1000 Hrs	FAIL

FIGURE 32; TABLE 4 – Hydrogen Embrittlement Set 1

This set shows that there is no direct embrittlement in any variation, however the bars exposed to salt spray all showed failure. Salt spray exposure is not generally regarded as a method for testing in-service embrittlement. As discussed earlier, salt spray is highly aggressive toward zinc. Therefore, this length of exposure may be an unrealistic re-embrittlement test. In addition, this experiment did not contain adequate controls.

A second set of bars were tested which included a broader range of variables and controls. This again included grit blast versus zinc phosphate preparation. The zinc rich primer here was the new charcoal optimized formulation. A duplicate set was tested with electrocoat only and no zinc primer as a control situation. The electrocoat in this set was gray color formula. Cadmium was also included as control. Several exposure environments were used including 500 hours B117 salt spray, 42 cycles GM9540P cyclic corrosion, and 1000 hours of condensing humidity at 100°F. Results are shown in Figure 33. Bar sets 9-12 were intended to show aluminum rich topcoat results, but were incorrectly processed and excluded from the data set.

Bar Set	Prep	Primer	TC	Exposure	Comments
1	Blast	none	E-Coat	none	PASS
2	C700C59	none	E-Coat	none	PASS
3	Blast	none	E-Coat	500 Hrs B117 SS	PASS
4	C700C59	none	E-Coat	500 Hrs B117 SS	PASS
5	Blast	none	E-Coat	42 Cy GM 9540P	FAIL 13.2 and 66.5 hrs.
6	C700C59	none	E-Coat	42 Cy GM 9540P	FAIL 16.3 and 198.8 hrs.
7	Blast	none	E-Coat	1000 Hrs. Cond. Humidity 100°F	PASS
8	C700C59	none	E-Coat	1000 Hrs. Cond. Humidity 100°F	PASS
13	Blast	Zn Rich	E-Coat	none	PASS
14	C700C59	Zn Rich	E-Coat	none	PASS
15	Blast	Zn Rich	E-Coat	500 Hrs B117 SS	PASS
16	C700C59	Zn Rich	E-Coat	500 Hrs B117 SS	PASS
17	Blast	Zn Rich	E-Coat	42 Cy GM 9540P	PASS
18	C700C59	Zn Rich	E-Coat	42 Cy GM 9540P	PASS
19	Blast	Zn Rich	E-Coat	1000 Hrs. Cond. Humidity 100°F	PASS
20	C700C59	Zn Rich	E-Coat	1000 Hrs. Cond. Humidity 100°F	PASS
21	Cd/Cr	none	none	none	PASS
22	Cd/Cr	none	none	500 Hrs B117 SS	PASS
23	Cd/Cr	none	none	42 Cy GM 9540P	PASS
24	Cd/Cr	none	none	1000 Hrs. Cond. Humidity 100°F	PASS

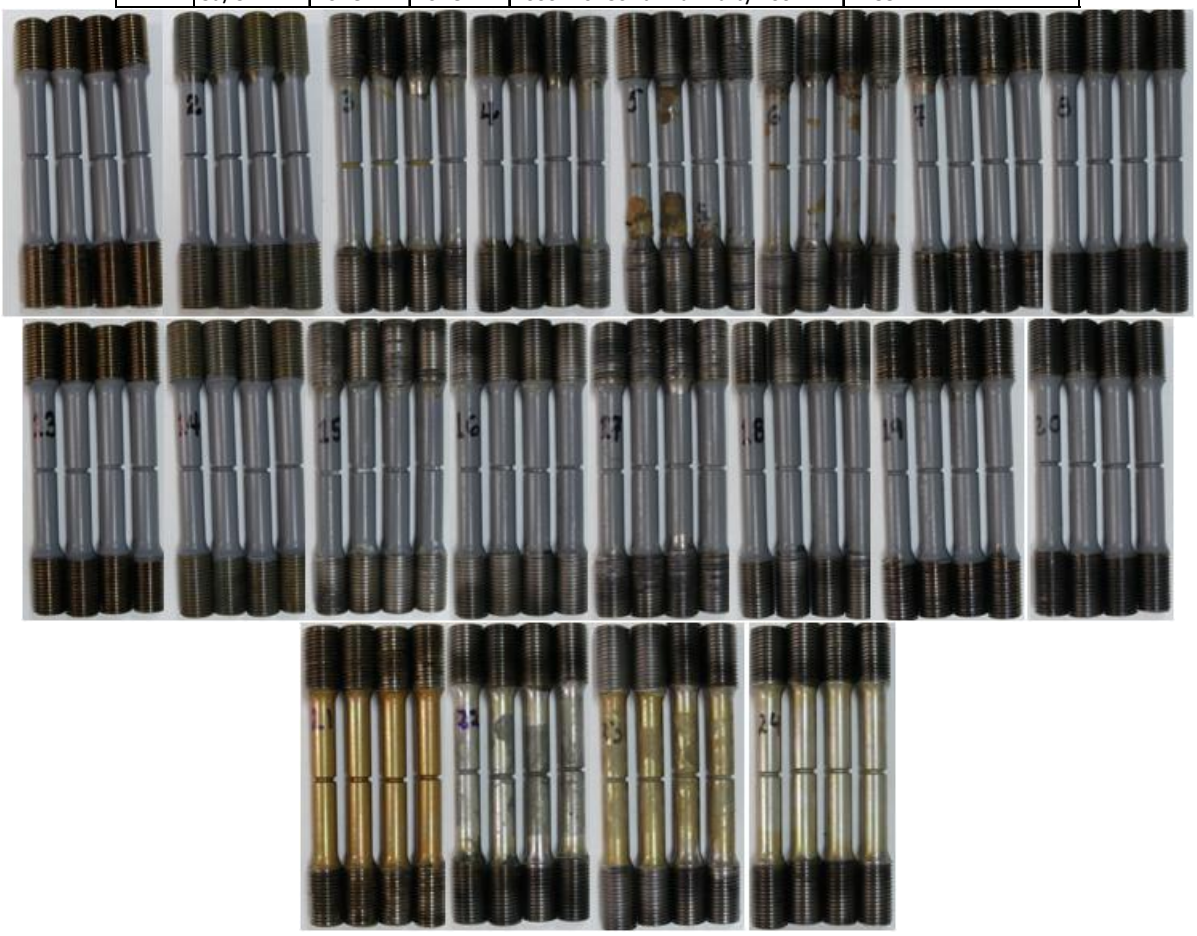


FIGURE 33; TABLE 5 – Hydrogen Embrittlement Set 2

This set shows, as did the first set, that there is essentially no effect due to the surface treatment variations. All bars passed tension testing with the exception of sets 5 and 6; electrocoat only after GM9540P exposure. It is possible that this failure was due to the greater than expected degree of red corrosion on these samples. Attempts were made to mask the threads on this set were inadequate to prevent corrosion of the bare steel and subsequent creep. However, this does not necessarily explain why this would affect the notched area where there was not excessive corrosion. It is important to note that all variants with zinc rich primer passed tension testing.

It is reasonable to conclude that the zinc rich and electrocoat processes of this coating system do not cause direct hydrogen embrittlement. However, the issue of in-service embrittlement is complex, especially for sacrificial coatings. This is an area where further testing is needed.

Torque-Tension – Ford Method WZ101 110607

Torque tension testing was done to automotive specification (GM and Ford) with spec. M10 test bolts. Torque modifier levels were adjusted in the E-Coat and aluminum rich topcoat formulations to meet these specifications. Work was done to demonstrate that these topcoats can be adjusted to meet other requirements for specific applications. Table 6 lists typical values for these optimized formulations. Cadmium is included for reference. Table 7 lists typical coefficient of friction (C.O.F) values.

Test Specification	Target	Zn Rich + E-Coat Topcoat	Zinc Rich + Al Rich Topcoat	Cd/Cr Control
Ford WZ101 WSS-M21P44 A3	48.8 ± 8 Nm @ 28.3 tension	46.5±1.5 Nm	42.6±3.5	--
General Motors GMW3359	46.3 ± 8.7 Nm @ 25.3 tension	48±8 Nm	43±1.5	39±6.2

TABLE 6 – Torque / Tension Values

GM (GMW3359)		Ford (WZ101)	
Torque	C.O.F.	Torque	C.O.F.
48.1	0.130	51.0	0.153
48.2	0.130	52.6	0.158
48.2	0.140	50.8	0.152
50.6	0.135	51.5	0.154
50.8	0.135	51.2	0.153
50.1	0.130	52.6	0.158
51.2	0.130	53.5	0.161
49.0	0.123	51.4	0.154
51.8	0.131	52.3	0.157

TABLE 7 – Coefficient of Friction Values

Torque / Tension testing passed standard automotive requirements with the multilayer approach and were not adversely affected by the zinc rich coating. The appearance and smoothness were found to be acceptable.

Electrochemical Characterization – ASTM G5-94

The plot in Figure 34 shows the open circuit potential and polarization curves of bare cold rolled steel (CRS), cadmium plated CRS, bare electrogalvanized CRS, zinc rich (ZRC) over CRS, and zinc rich over zinc phosphated (C700C59) CRS. By definition, the Open Circuit Potential is the potential difference between your test piece (working electrode) and the reference electrode (in our case Ag/AgCl) of constant electrochemical potential, in a common electrolyte, at which no current flows. As expected, pure zinc (galvanized) is more sacrificial to steel than cadmium. The zinc rich over bare CRS and over zinc phosphate are very close in sacrificial potential to electrogalvanized zinc. This indicates that the zinc rich primer has substantial electrical continuity within the zinc layer as well as good contact between the zinc and steel substrate, even through the zinc phosphate layer.

The plot line for zinc rich primer over zinc phosphate has a different shape than the primer over bare steel. When scanning potentials increase above the OCP (the anodic branch), it is possible to go through a finite region or regions where the current flow stops increasing with potential difference or even decreases with potential difference increase (e.g. the ZRC over phosphate). This passive region is a region where there is a loss of electrochemical reactivity such as would happen when a chemical modification of the surface occurs, which limits corrosion. The potentiostat used here has an upper current density measurement of 1×10^{-3} A/cm2. Because the phosphate layer acts as an insulator, it is possible to collect data to a higher potential difference since the current flow stays within a measurable range. The passive region is probably present for all primers. It may be a region where the zinc particles near the surface have been oxidized and the potential difference is not great enough to oxidize zinc particles below the surface. Once the potential difference overcomes this resistance, current flows again.

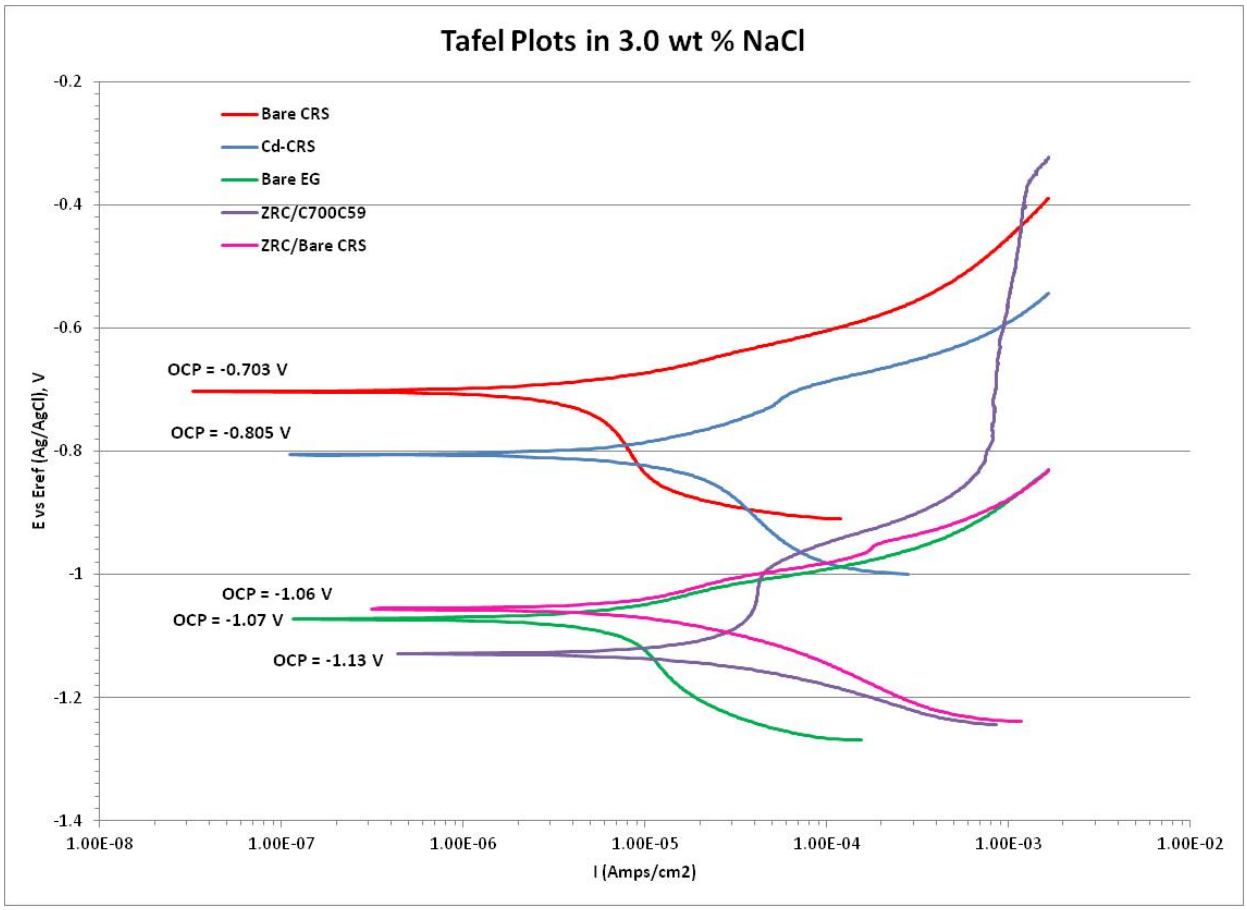


FIGURE 34 – Tafel Plot - Open Circuit Potential

Commercialization

The coatings developed in this work are now considered to be commercially available for sale. Concurrent with this effort, the materials and methods of manufacture have been screened for workability within the production capabilities of PPG. The raw materials as well as the final product have been screened for environmental and toxicological hazards. MSDS sheets are available. In addition, commercial supply chain for all raw materials has been secured.

In the coming months, we will be producing production scale batches of the zinc rich primer and the aluminum rich topcoat. These will be used for a production scale application trial (automotive parts). Previously, production scale trials with the zinc rich primer plus electrocoat have been performed for automotive customers with excellent results.

The electrodeposition topcoat is currently available at major fastener applicators for full scale bulk production. PPG is prepared to coordinate the design, engineering, installation, and operational support for any new electrodeposition and/or dip-spin application systems of any size and level of automation. The topcoats can also be reformulated to meet specific colors and torque requirements.

The zinc rich material is currently being used commercially in a pilot dip-drain operation. Results are positive and full production is expected in coming months.

We are prepared to process parts submitted by any DoD (or industrial) end user for testing purposes. The commercial codes and names are as follows:

Zinc Rich Primer – SPR67868A – SPINCOAT™ ZRC, SPECTRACRON® ZR
Aluminum Rich Topcoat – SEP70859, SPINCOAT™ AR
Electrodeposition Topcoat - POWERCRON® XP

Zinc Rich plus E-Coat System – ELECTROPOLYSEAL® IV
E-Coat only over zinc phosphate – ELECTROPOLYSEAL® III

Approvals – Currently, PPG cationic electrodeposition primers have broad global automotive OEM approval for bodies and parts. The torque modifies Powercron XP has automotive OEM approvals for fastener coating directly over zinc phosphate (ELECTROPOLYSEAL III). Submissions of the zinc rich plus electrocoat fastener coating have been made to several automotive customers globally. Specification testing has been underway and approvals are imminent.

A gray version of PPG epoxy cationic electrocoat has received approval to MIL-P-53084 and meets requirements of A-A-52474A. A black version has been submitted for approval as well. There are currently no approvals for the multilayer fastener coatings described here.

We have taken some steps to begin the process of introducing these coatings to the DoD user community, and achieve MIL spec approvals. In conjunction with the Army Research Lab (ARL), we have submitted a pre-proposal to ESTCP for demonstration and validation activities. This would include writing new specifications for zinc rich coating plus electrocoat for fasteners. In addition, we have submitted coated samples to Oshkosh Truck for testing. We are also engaged in ongoing conversations with Navy personnel about use of electrocoat and zinc rich primers in shipyards.

We will also use the CorrDefense web portal (www.corrdefense.org) to aid in the product introduction process.

Conclusion

A multilayer coating system for fasteners and other components has been developed which exhibits excellent corrosion resistance. This coating represents a viable, environmentally friendly alternative to cadmium/chromium coatings for high strength fasteners. The primary system includes zinc phosphate conversion coating, dip-spin application of an inorganic zinc rich primer, followed by an epoxy topcoat applied by cationic electrodeposition. An alternative aluminum rich topcoat has also been developed for dip-spin application where electrocoat is not available. Both coating systems meet the goals of minimum 1000 hours of salt spray performance. Both also meet torque/tension requirements. Both are free of cadmium, chromium, lead, and nickel. The electrodeposition topcoat offers an environmentally benign coating alternative and is an excellent method for bulk application such as fasteners.

The coatings and processes have been tested in production scale environments and are ready for commercial distribution. Testing and approvals to automotive, industrial, and construction specifications is underway with very positive results. The zinc rich plus electrocoat finish has been used commercially in a dip-drain application successfully.

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Publications and Presentations

1. Presentation and technical paper - NACE 2009 DoD Corrosion Conference (8/2009)

   http://www.corrdefense.org/Technical%20Papers/ZINC%20RICH%20COATINGS%20FOR%20FASTENERS.pdf

2. Presentation at ASETSDefense Workshop 9/2009)
3. Presentation and technical paper (same as NACE) - PACE 2010 DoD Corrosion Conference (2/2010)
4. Presentation to NSPR Panel 3 (2/2010)
5. Presentation at Mega Rust 2010 (6/2010)