Paper #17

An Enhanced Corrosion Protection Mechanism for Rubber-to-Metal Bonding

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Presented at the Fall 180th Technical Meeting of the American Chemical Society, Rubber Division
October 11-13, 2011
Cleveland, Ohio

ISSN: 1547-1977

Abstract:

An Enhanced Corrosion Protection Mechanism for Rubber-to-Metal Bonding

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The trend toward more stringent performance requirements for many transportation and industrial applications poses a significant and potentially costly problem for elastomeric bonding to various metal substrates. This paper addresses a new process which enhances the long-term corrosion characteristics of rubber-to-metal bonded components while improving bond strength at the same time.

This paper details new results of of a thermo-diffusion coating that works by Thermo-Chemical Surface Modification (TCSM) . This diffusion process forms a protective layer that partially diffuses into the substrate and cannot be separated by physical or environmental testing. Following surface modification, application by spray, dip, or dip-spin of an engineered waterborne air-dry/low-bake coating adds additional functionality; yielding over 2000 hours of salt spray corrosion with no visible evidence of rust or oxidation.

The complimentary technologies for thermo-diffusion and waterborne coatings yield high performance synergies for bonding adhesion and corrosion protection using environmentally friendly products and processes that are compatible with industry recognized polymer based adhesives. The system is ideal for rubber to metal bonding applications since the material enhances bond strength with decreased potential for failure, while offering better overall appearance and part performance.

1.0 MOTIVATION

Performance standards, especially in the automotive market, continue to become more stringent. When was the last time you saw a rusted-out car? Even under-hood or under-carriage components which normally escape scrutiny are now subject to demanding finishing requirements. The term *cosmetic corrosion* defined as “corrosion that occurs as a result of the breakdown or damage to a coating system. Typically, this type of corrosion does not impact function but does compromise appearance” is now an integral part of various automotive specifications (e.g. SAE J2334).

Not only do part suppliers need to produce components that meet tighter functional and cosmetic standards, but they must do so with environmentally compliant technology, and at a competitive cost. For a wide range of components that require elastomeric bonding, such as engine mounts, vibration dampeners, and similar assemblies, this has meant having to search for a better mousetrap.

The “just paint it black” approach, with cursory pretreatment that allowed manufacturers to meet 100 or 200 hours of salt-spray resistance in the past no longer suffice when faced with 1000 hour testing, thermal shock, and other advanced tests.

At the same time, controls on heavy-metal chemistries including the prohibitions on the use of trivalent and hexavalent chrome have motivated producers to find “green” technologies that have more eco-friendly chemicals. This same environmental tide has prompted paint formulators to abandon solvent laden paints with high VOCs for waterborne materials that are safer to use, easier to apply and clean up, and have better overall cost-efficiency.

This paper presents a new approach to protecting ferrous and ferrous-alloy under-hood and under-carriage, components; and in particular the two dozen or so on each vehicle that require rubber-to-metal bonding processes. This novel solution combines the beneficial aspects of two separate processes. First, a thermal diffusion mechanism that provides exceptional corrosion resistance through surface modification that produces a zinc-aluminum-iron diffusion layer with sacrificial coating properties. This is followed by the application of a durable, waterborne coating that adds additional corrosion protection and a pleasing cosmetic appearance. Figure 1 illustrates the various components that comprise the finished part.

We are able to achieve a uniform film thickness across all facets of surface even for complex part geometries that include challenging sharp edges, recesses, and threaded surfaces that are common to rubber-to-metal bonded components.

The system meets, and exceeds current and proposed OEM standards, and is ideal for rubber-to-metal boding applications where test results demonstrate not only superior corrosion protection and appearance, but better initial bond strength, better bond strength retention, and less variability than obtained with the conventional processes.

Manufacturers of molded rubber-to-metal components can implement lower cost alternatives for corrosion protection and metal prep operations. Various types of electroplating (Zn & ZnNi) or electro coatings (E-Coat) applied to substrates for corrosion protection that interfere with the adhesive bonding systems can be exchanged for a combination of coatings that promote process flexibility and performance.

2.0 THERMAL DIFFUSION PROCESS DESCRIPTION

The Greenkote® thermo-diffusion batch process utilizes a dry bulk powder formulation that creates a uniformly applied Zn-Fe-Al sacrificial coating. Its unique anchor patterns improve the adhesion of top coat layers such as those used for primer and adhesive bonding systems and promote improved under-bond corrosion protection. Test results demonstrate this adhesion exceeds that of conventional auto-deposition, e-coat or plating technologies.

The zinc/aluminum coating can be applied as a base coat from 20µ to 50µ on a broad range of ferrous metals and alloy combinations used for stampings, fasteners, shapes, castings, and forged components. The coating is intended to replace zinc or iron phosphate pretreatments and abrasive cleaning on non-heat treated metal substrates. The thermo-diffusion process does not contain Chrome III or Chrome VI, does not cause Hydrogen embrittlement and is fully compliant with RoHS and ELV Directive (2000/53EC).

The coating is compatible with a wide range of the most popular one- and two-coat adhesive products used for molded rubber compounds formulated from natural and synthetic elastomers. The coating forms a hard surface that improves adhesion of primers and adhesives and promotes improved bond strength. Increases in both initial bond strength and bond strength retention are evidenced by repeatable elastomer fracture during destructive bond testing (as detailed in Section 5.0).

The thermo diffusion process is described pictorially in charts 2a, 2b and 2c which illustrate the two phases of the diffusion process and resulting coating structure.

In the first phase, (Figure 2a) dry metal zinc (Zn) and aluminum (Al) powders are thermally diffused in a retort, in the presences of the ferrous substrate. The differences in melting temperatures create a dynamic process in which first, zinc is diffused into aluminum powder and iron on the substrate surface. Aluminum is diffused into zinc particles and a zinc-iron diffusion layer is created. A Zinc-Aluminum powder with a lower melting point is created.

As the diffusion process continues (Figure 2b) in the second phase, the Zn-Al powder melts and is absorbed onto the Zn-Fe diffusion layer. Further diffusion by zinc into the Zn-Fe layer as well as Fe from the substrate into the Zn-Al grains continues to propagate. This results in the creation of Al-rich areas which serve to bridge voids and fissures in the surface.

Microscopic photos of the resulting surface and cross section are illustrated in Figures 3a and 3b respectively.

Figure 2c illustrates the final 10 to 100 Micron coating structure comprised of a zinc rich poly metal combination (Zn-Al-Fe) with aluminum filled inclusions over Zn-Fe diffusion layer that protects the ferrous substrate. The finished surface is protected, with an applied coating that is not prone to blistering, chipping, loss of adhesion, water infiltration and other problems related to a substrate-chemical interface, but rather is a surface modification which becomes integral to the part.

The thermal diffusion coating provides an excellent surface for popular rubber-to-metal primers and adhesives, providing superior adhesion and underbond corrosion protection. Test results indicate 20% to 30% greater initial bond strength as well as more consistent results (as documented in the test results section 5.0 below).

Importantly, there is also significantly improved bond strength retention of elastomeric parts after 1000 hours of salt spray exposure. This means that not only does the process improve the rubber-to-metal performance of bonded parts, but these parts continue to perform under severe exposure where conventionally produced parts fail.

Figures 5a and 5b illustrate the difference in corrosion for test parts treated with both traditional iron phosphate and a thermal diffusion layer that have been subsequently coated with bonding adhesive. The parts are scribed and subjected to corrosion testing. While there is failure of the adhesive on the phosphate treated substrate, there is no failure on the thermal diffusion panel.

While thermal diffusion produces a more durable, corrosion resistant part with better rubber bond strength performance, the part surface does contain metals that are prone to oxidation after the thermal diffusion process. The presence of iron in the diffusion layer manifests itself during salt fog testing as red blush to the surface, while the presence of aluminum and especially zinc oxides appear as a white discoloration of the surface that some consumers may find objectionable. Figure 5b is typical of this appearance. This cosmetic corrosion differs from systemic corrosion in that the underlying substrate itself is stabile and not diminishing in mass. However, since customer preference is for a part with no visible oxidation, a suitable paint top coating is desirable for both aesthetic and functional reasons.

As discussed below, the paint must have excellent inter-coat adhesion to the diffusion layer, since in rubber-to-metal bonding applications the adage “the chain is only as strong as the weakest link” is present at every interface.

3.0 WATERBORNE COATING PROCESS DESCRIPTION

The top coat is a water based low VOC polymer coating that provides excellent corrosion resistance with low moisture and vapor permeability properties.

Long term corrosion resistance to non-bonded surfaces are subsequently enhanced by top coating the thermal diffusion layer with the coating providing a durable finish at variable thicknesses based upon customer requirements. The material is formulated using a low vapor permeability resin system that combined with corrosion resistant pigments to provide a combination of superior adhesion and corrosion resistance. A complete technical specification is presented in Appendix 2.

Molded components and assemblies can be coated shortly after removal from molds and tooling with excellent adhesion to metal and rubber surfaces providing a low gloss black appearance. Coating application methods for the coating include spray, dip spin and dip/drain, providing excellent coverage that can be air dried within minutes for part handling. Exposure to low bake temperatures will accelerate dry times

The waterborne coating can be formulated for colors with gloss levels up to 35 (on a 60 degree gloss meter) and complies with several OEM specifications as a cost effective alternative for electro deposition coatings on metal surfaces. Laboratory corrosion studies for combinations of diffusion coating with waterborne top coat exceed 2000 hours as tested in accordance to ASTM B 117. High temperature versions are available as well.

Figure 4a illustrates the effect of the waterborne coating on improving the aesthetic appearance and corrosion protection of panels prepared with the diffusion process alone. The left hand test panel exhibits white zinc oxide corrosion, and shows some evidence of red blush due to the presence of iron in the diffusion layer. The right hand panel, top coated with waterborne paint shows virtually no signs of objectionable oxidation or corrosion. The coating can be custom formulated in a variety of colors for marking and coding requirements without loss of performance.

Figure 4c illustrates the results of test parts prepared with one- and two-coats of waterborne top coating to demonstrate that even at low coating weights (<<25 microns), parts have superior protection to parts coated with conventional systems but at much higher film builds. The combination diffusion / waterborne system helps to eliminate corrosion that reduces the metal mass of parts. This may have substantial cost implications since designers can reduce vehicle weight by utilizing lower mass, corrosion resistant components.

4.0 EMPIRICAL RESULTS AND TEST DATA

In this section we discuss results of testing on non-bonded and rubber-bonded test parts.

4.1. Tests on non-bonded test panels

This test demonstrates the long-term corrosion resistance (2,000 hours) of a thermally diffused coating with protective waterborne top coat on ferrous substrates. The goal is to test salt spray corrosion resistance far beyond the current OEM automotive criterion.

To evaluate the salt spray corrosion resistance properties of a system of coatings comprised of the PM-1 thermal diffusion coating with a top-coat of Kalgard® 094-line functional coating, steel test panels prepared using the thermal diffusion process, cleaned with the proprietary phosphate process, coated with the waterborne material and subjected to salt spray testing according to test method ASTM B117.

The test substrate is ACT 3”x5”x.032” cold rolled steel TRU® brand test panels. A Zn-Al-Fe diffusion coating was applied at a nominal coating weight of 25μ. Test panels were then given an additional proprietary phosphate rinse for passivation. The prepared panels were top-coated with a black water-reducible coating (#94-9218). Coating was applied by dip coating the panels to achieve a 25.0μ – 32.5μ DFT paint film build. The coated panels were air dried for the prescribed time prior to salt spray testing.

The prepared test panels were scribed and subjected to 2,000 hours of salt spray exposure in accordance with ASTM Standard B117 using a Q-Lab Q-Fog® salt spray enclosure. The panel edges were not taped. After air drying for the requisite time, the panels were added to a salt spray chamber and were evaluated at tape tested at 250 hour increments. The test panels were removed after 2,000 of salt spray exposure.

Panels were uniform in appearance at 250 hours, 500 hours, 750 hours and 2000 hours with little evidence of rust or corrosion on the face of the panel. They showed no loss of adhesion during any of these checks and no creep was observed along the scribe line and all panels passed a tape pull adhesion test on the scribed line. Corrosion occurred only near the edges of the panel (which were un-coated and un-taped) and the hole in the test panel. There was no noticeable blistering of the coating. A photograph of the final test panel is shown in Figure 4b below.

Figure 4c compares the performance of waterborne coating applied to conventional phosphate treated automotive parts with the same coating applied to diffusion coated parts after 720 hours of salt spray testing. This is observable corrosion on the parts prepared with phosphate, and little change to the thermal diffusion coated parts.

4.0.2 Test results on rubber-to-metal bonded parts

Two series of tests using different adhesive systems were conducted. In both a single coat adhesive primer followed by a single coat adhesive top coat were applied prior to molding using a 52 durometer rubber. Parts were tested for initial bond strength and then tested again for bond strength in accordance with ASTM D429 after 1,000 hours of continuous salt spray exposure in accordance with ASTM B117.

Table 1 and Table 2 present results for the first adhesive formulation.

Table 1 illustrates that while there is negligible difference in creep, corrosion and blistering between the diffusion process and conventional system at 500 hours, that there is substantial difference in performance at 1,000 hours.

Table 2 illustrates the impact of under-bond corrosion on bond failures. The diffusion coatings exhibit a higher initial bond strength (+22.35%, and +26.96% respectively) compared to conventional Phosphate. After 1000 hours of neutral salt spray, the diffusion coatings retain a substantially higher percentage of their initial performance and have 285.5% higher bond strength than the current protection system. The diffusion coating loses -15.45% of initial strength, the PM-10 loses -18.04% of initial strength while the zinc phosphate treated parts lose -73.16% of initial bond strength (with a significant amount of under-bond visible corrosion). Note that the process variability (expressed by the standard deviation) is significantly higher for the conventional phosphate process compared with the relatively consistent diffusion coating treatments.

Similar bond failure results are reported in the second trial and are presented in Table 3. There is significant improvement in the initial bond strength (+21.71%) using the diffusion process. Again we find strikingly higher improvement in bond strength following 1,000 hours of corrosion exposure (+93.9%). We again report substantially better bond strength retention (-17.8%) compared with the current protection mechanism (which fell 43.6%). This trial also illustrates a dramatic reduction in variance of failures as evidenced by the standard deviations in each trial.

5.0 CONCLUSIONS AND FUTURE DIRECTION

To meet increasingly stringent requirements for durability and aesthetics rubber-to-metal bonded parts require an environmentally compliant technology that provides salt spray corrosion in excess of 1000 hours and does not show signs of oxidation (e.g. red blushing).

A new system comprised of a thermal diffusion coating which provides a sacrificial barrier and waterborne corrosion resistant paint provides the combination of properties required by industry.

The system provides several benefits over conventional technology:

1. Improved corrosion protection, exceeding 1,000 hours of ASTM B117 salt spray, with up to 2,000 hours in testing.

2. Improved initial bond strength performance, greater bond strength retention, and less variability in bond strength. No visible corrosion beneath the bonded surface.

3. Thin, uniform coating weight for close mechanical tolerance applications.

4. Eco-friendly solution with no dangerous Chrome III or Chrome VI materials

5. Protection of complex surfaces with difficult to coat geometries.

The process is robust, environmentally compliant and cost-efficient; presenting manufacturers with an opportunity to produce parts conforming to OEM requirements.

6.0 APPENDIX: FIGURES

Figure 1. Cross section of part with diffusion coating, adhesive primer, top coat, bonded rubber, and waterborne coating.

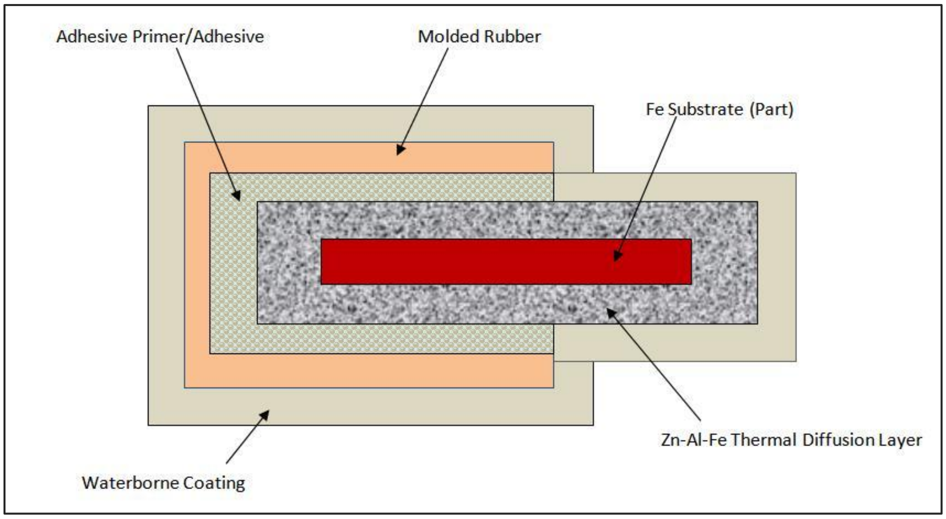
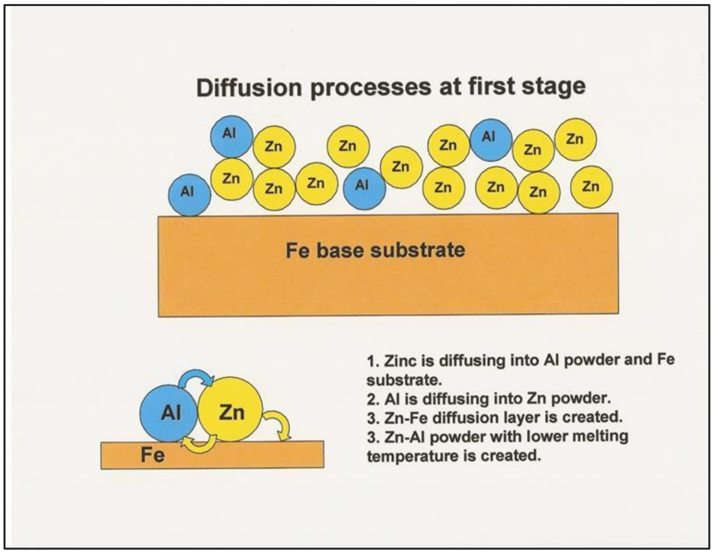
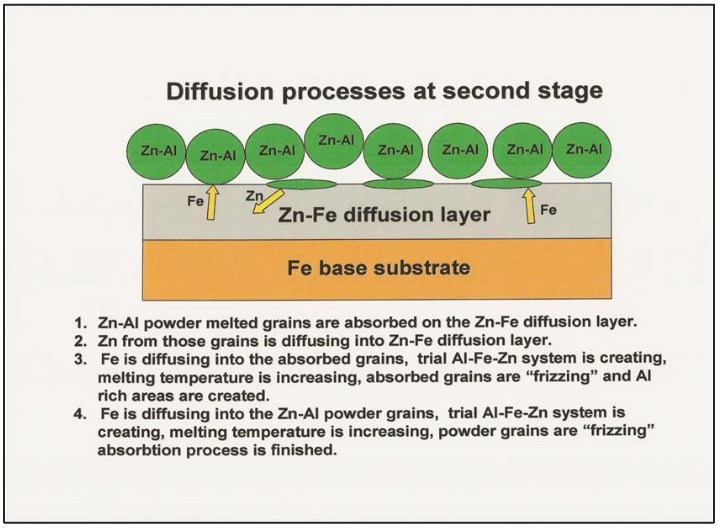


Figure 2a. Thermal Diffusion Process – Stage One


Diffusion processes at first stage

1. Zinc is diffusing into Al powder and Fe substrate.
2. Al is diffusing into Zn powder.
3. Zn-Fe diffusion layer is created.
3. Zn-Al powder with lower melting temperature is created.

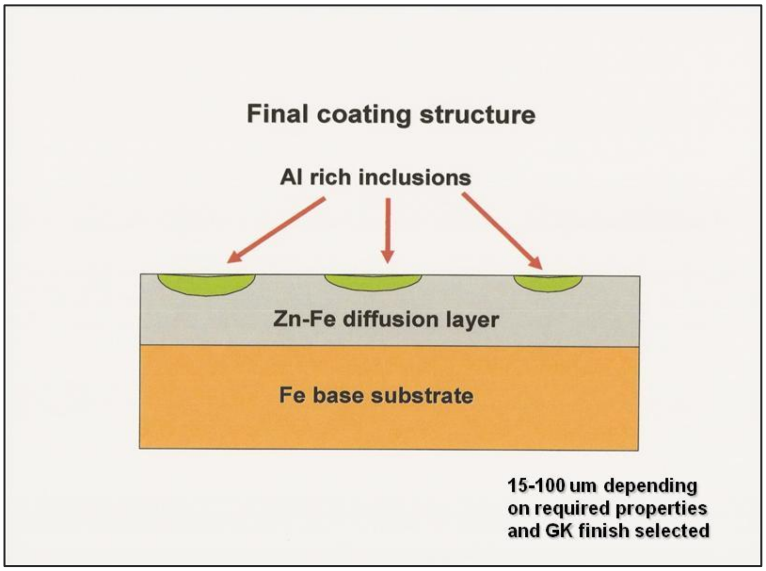
Figure 2b. Thermal Diffusion Process – Stage Two



Diffusion processes at second stage

1. Zn-Al powder melted grains are absorbed on the Zn-Fe diffusion layer.
2. Zn from those grains is diffusing into Zn-Fe diffusion layer.
3. Fe is diffusing into the absorbed grains, trial Al-Fe-Zn system is creating, melting temperature is increasing, absorbed grains are “frizzing” and Al rich areas are created.
4. Fe is diffusing into the Zn-Al powder grains, trial Al-Fe-Zn system is creating, melting temperature is increasing, powder grains are “frizzing” absorbtion process is finished.

Figure 2c. Thermal Diffusion Process – Final Coating Structure



Final coating structure

15-100 um depending
on required properties
and GK finish selected

Figure 3a. Micrograph of Diffusion Coating Surface Area

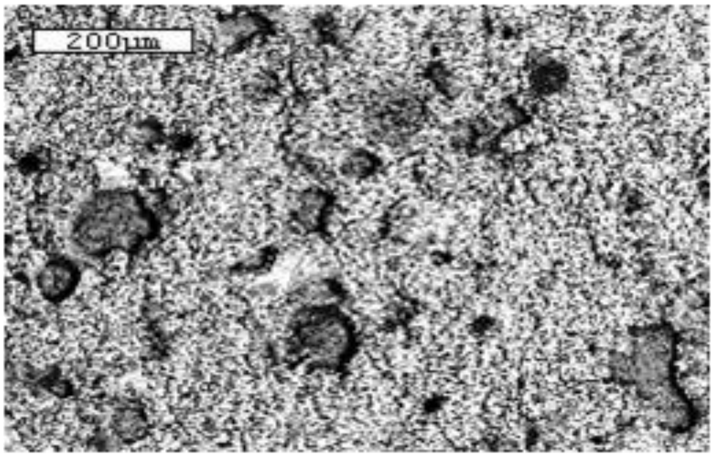


Figure 3b. Micrograph of Thermal Diffusion Coating – Cross-Section

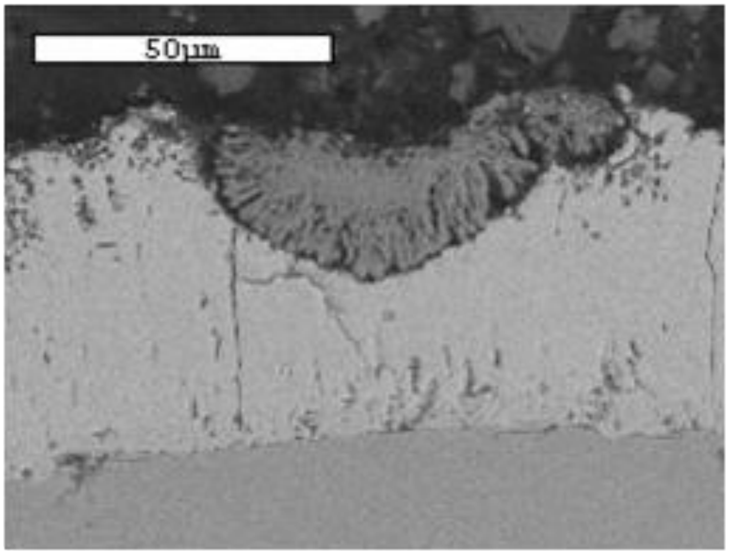


Figure 4. Non-bonded Corrosion Test. 2,000 hours ASTM B117 Salt Spray.

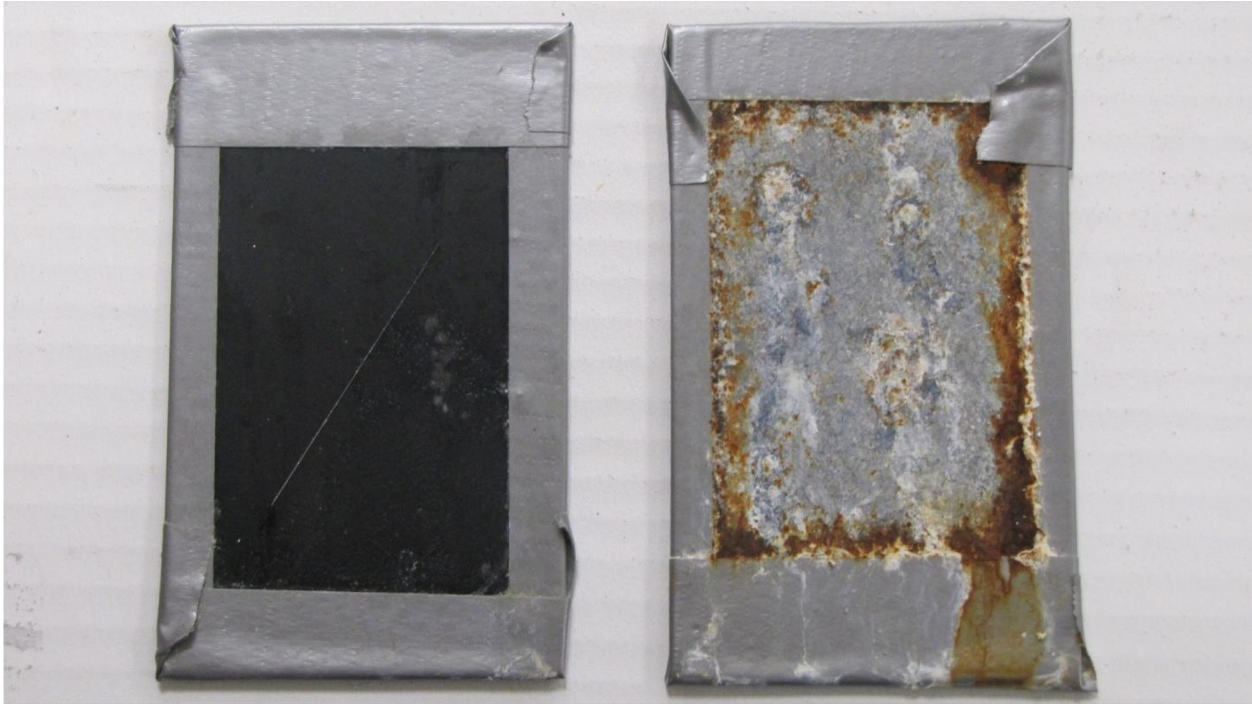


Figure 4b. Non-Bonded Panel after 2,000 hours of exposure. Thermal Diffusion Coating with waterborne top coat

4c. Waterborne Coating with Phosphate vs. Thermal Diffusion: 720 hours ASTM B117 Salt Spray

Table 1. Results of Greenkote/Bonding Adhesive -Panel Study 1. Corrosion, Creep and Scribe.

	Scribe Creep (mm)		Blistering		Unscribed Area	
Treatment	500 h	1000 h	500 h	1000 h	500 h	1000 h
Greenkote PM-1	0	0	none	none	No failure	No failure
Greenkote PM-10	0	0	none	none	No failure	No failure
Zinc Phosphate	0.1 mm	> 16 mm	none	several	No failure	5% Failure

Table 2. Results of Bonded-Test Bar Study 1. Bond Strength.

	Initial Bond Strength		1000 Hours Salt Spray		
Treatment	Pounds	Std. Dev.	Pounds	Std. Dev.	% Change
Greenkote PM-1	1150.0	18.9	972.7	25.5	-15.42%
Greenkote PM-10	1193.3	35.3	978.0	72.2	-18.04%
Zinc Phosphate	939.9	104.8	252.3	253.5	-73.16%
Improvement (w/PM-1)	+22.35%		+ 285.5%		

Table 3. Results of Bonded- Component Study 2. Bond Strength.

	Initial Bond Strength		1000 Hours Salt Spray		
Treatment	Newtons	Std. Dev.	Newtons	Std. Dev.	% Change
Greenkote PM-1	6831.5	169.49	6138.0	276.6	-10.15%
Zinc Phosphate	5613.0	1971.0	3165.0	1858.0	-43.61%
Improvement	+ 21.71%		+ 93.93%		

Figure 5a: Iron Phosphate with Adhesive top coat following 1,000 hours salt spray

Figure 5b. PM-1 Thermal Diffusion with adhesive top coat following 1,000 hours salt spray

APPENDIX 2: WATERBORNE COATING TECHNICAL SPECIFICATIONS

Product Name	Kalgard 094 – water reducible coating #94-9218JB
Solids	54% ±2% by weight, 37% ±2% by volume
VOC	0.5 lbs/gallon theoretical
Weight/Gallon	11.12 ± 0.2 lbs / gallon
Viscosity	35 ± 2 seconds, #2 Zahn
Flash Point	205°F
Gloss	2 – 8 @60°
pH	5.5 – 6.5
Coverage	303 sq. ft. / gallon @ 2.0 mil DFT
Salt Spray	500+ hours ASTM B117
Humidity	480+ hours ASTM D2247
Gravelometer	Pass, SAE J-400
Chemical Resistance	50/50 Ethylene Glycol, Excellent
	10w30 Engine Oil @275°F @ 1 hour, Excellent
	Gasoline 70°F @ 1 hour, Excellent
	Brake Fluid 70°F @ 1 hour, Excellent
Self Life	6 months maximum @ 70°F
Cure Schedule	30 minutes @ 75°F @ 50% RH to Touch
	45 minutes @ 75°F @ 50% RH to Handle
	4 hours @ 75°F @ 50% RH to Recoat
Application	Spray (air, airless, electrostatic), dip, dip spin, brush touch-up
Clean-up	While plastic: warm detergent water, after cure: MEK