Trivalent Chromium-based Post-treatment for Sacrificial Coatings

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A novel trivalent chromium-based post treatment shows excellent performance compared to hexavalent chromium-based post treatments. When used as sacrificial coatings, metals such as cadmium, zinc, aluminum, and zinc- and aluminum alloys require a supplemental coating to maximize corrosion resistance. Typically, the best corrosion performance is achieved with coatings formed from chromate or hexavalent chromium compositions. Non-chromate alternatives to date have been unable to match or beat the performance of chromate post treatments and, as a result, most sacrificial coatings, when used in severe service environments, are still specified with a chromate post treatment. Trivalent chromium post treatment compositions and processes (TCP) developed by NAVAIR perform as well as or better than standard chromate post treatments in corrosion resistance. TCP coatings on Cd, IVD Al, Zn-Ni and Sn-Zn show equivalent performance to chromate coatings in a 1000-hour scribed neutral salt fog test. An improved version of TCP with a color change additive shows superior unscribed corrosion performance on IVD Al, with some test coupons lasting three times as long as any other coating before the onset of red rust. TCP can be applied by immersion, spray or wipe at ambient conditions with typical contact times of 10 min. The TCP coating requires no other processing or post treatment for optimum performance.

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Introduction

Components and systems used in defense, aerospace, automotive, marine and other applications rely on protective coating systems for resistance to corrosion and other forms of degradation. Parts of these protective coating systems can include corrosion inhibiting organic primers and topcoats, sealants, corrosion protecting compounds, and inorganic coatings.

There are a number of inorganic coatings available for corrosion protection, the selection of which is based on the substrate to be protected, the severity of the operating environment, the life-cycle cost of the coating, and more recently, environmental considerations. Aluminum surfaces can be conversion coated, phosphated, anodized, or coated with sacrificial or barrier coatings. Steel surfaces can be phosphated or coated with sacrificial or barrier coatings.

For steel, metallic coatings that yield barrier and galvanic (sacrificial) protection are the highest performing and are described in a number of commercial and military specifications where maximum corrosion resistance is necessary[1-5]. These coatings are then used as coated or further protected with a variety of organic coatings. Table 1 describes the most commonly used materials and the types of components or surfaces on which they are used.

Table 1: Sacrificial Coating Type and Common Usage

Coating	**Specifications**	**Applications**
Cadmium	AMS QQ-P-416	General use; including high-strength steels; excels in Cl^- environment
Zinc	ASTM B 633	General use; not used on high-strength steels due to in-service embrittlement; excels in industrial environment
Zinc-nickel	AMS 2417	General use; used in selected cases on high-strength steels with Ni strike
Tin-zinc	AMS 2434	General use; corrosion performance typically moderately inferior to Zn-Ni coatings
IVD aluminum	MIL-C-83488	General use; including high-strength steels; excels in Cl^- environment

Historically, the least expensive, most widely used sacrificial metallic coating for environments where chloride species are present is cadmium. Zinc is the metal of choice for industrial environments[6]. While zinc remains the workhorse protective coating for industrial applications, cadmium has been a target for replacement because it is carcinogenic. Commercially available alternatives to cadmium are all generally based on aluminum or zinc. Ion Vapor Deposited (IVD) aluminum is used on defense aviation components like landing gear, and zinc alloys like zinc-nickel and tin-zinc are being implemented in a variety of applications that are not susceptible to embrittlement during use.

A common thread for all of these coatings is the need for a high-performance supplementary "post treatment" that deposits a coating which maximizes corrosion performance and paint adhesion for a given coating. For all materials, the best-performing post treatments are produced from aqueous hexavalent-chromium containing solutions. The resulting coatings contain hexavalent chromium as well.

The United States Naval Aviation Systems Command (NAVAIR) has developed alternatives to hexavalent chromium post treatments for zinc and zinc alloys, aluminum and aluminum alloys and cadmium. One class of alternatives is based on trivalent chromium chemistry (TCP)[7]. A second class is based on non-chromium chemistry (NCP). Performance data for the trivalent chromium post treatment processes will be presented here. Data for the non-chromium processes will be reported at a later time.

Results

Experiment 1

Electroplated cadmium, tin-zinc, zinc-nickel, and Alumiplate, and IVD aluminum coatings were supplied by the organizations noted in Table 2. All coatings are deposited directly onto the steel substrate except for Alumiplate, which has a sulfamate Ni strike. Each organization post treated a set of each coating with their standard hexavalent, or "chromate," process. A second set was sent to NAVAIR and coated with TCP. The tin-zinc and zinc-nickel specimens were activated by immersing the coatings in 5% sulfuric acid for 30 seconds immediately prior to processing with TCP. TCP was spray applied to the cadmium, tin-zinc and zinc-nickel coatings with a five-minute dwell time. After the dwell, coatings were thoroughly rinsed in tap water followed by a deionized water rinse. The Alumiplate and IVD aluminum were immersion processed. TCP was applied to Alumiplate without activation, using a 10-minute dwell. TCP was applied to IVD aluminum using a 5-minute dwell. The IVD aluminum coating was activated using a 30-second immersion in an iron-based, non-chromate deoxidizer. All coatings air dried at ambient conditions for a minimum of 24 hours before subsequent use. TCP is similar to chromate coatings in that a dehydration period is necessary for proper coating formation and performance. Figures 1 through 5 detail coating appearance after post treatment with chromate and TCP.

Table 2: Sacrificial Coating Supply

Coating	**Supplier**
Cadmium	NAVAIR Patuxent River
Zinc-nickel	Courter-Hall, Dipsol Gumm process
Zinc-nickel	Boeing, Boeing process
Tin-zinc	Boeing, Dipsol Gumm process
Alumiplate	Alumiplate
IVD aluminum	Naval Aviation Depot North Island

Figure 1: Alumiplate with chromate (R) and TCP (L)

Figure 2: IVD Al with chromate (R) and TCP (L)

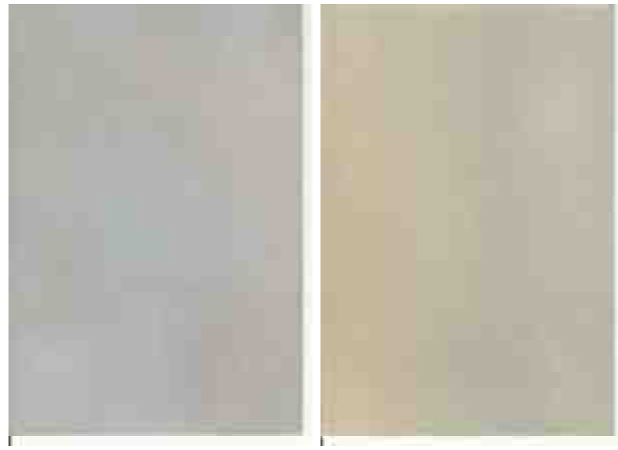


Figure 3: Boeing Zn-Ni with chromate (R) and TCP (L)

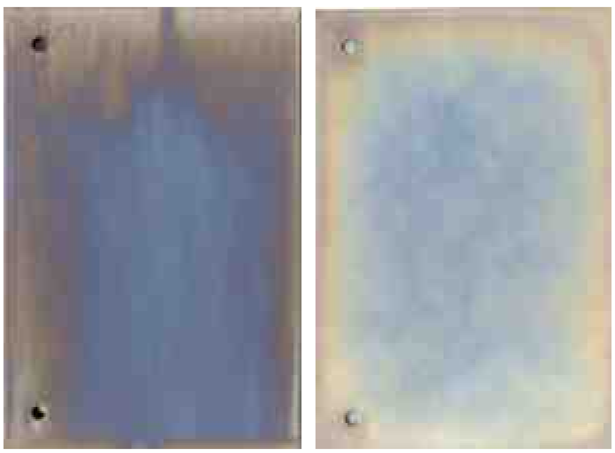


Figure 4: Dipsol Gumm Zn-Ni with chromate (R) and TCP (L)

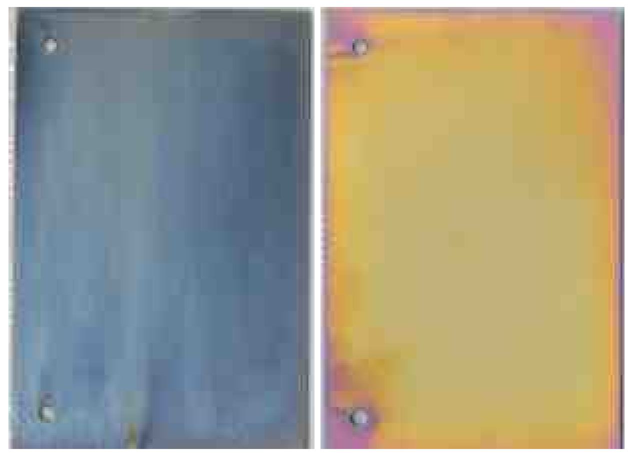


Figure 5: Cadmium with chromate (R) and TCP (L)

Coatings were manually scribed with a carbide-tipped stylus and subjected to 1000 hours of neutral salt fog per ASTM B 117. This test, along with an unscribed 3000 hour neutral salt fog test are basic tests used by NAVAIR and other organizations to evaluate the performance of sacrificial coatings on steel.

Figures 6 through 11 detail the relative performance of each coating system. For this test, the important comparison is TCP versus chromate post treatment for each coating. As shown in the figures, the TCP performs similar to the chromate post treatments. For the cadmium, the TCP showed coating discoloration, but this is not a cause for failure since the appearance of red rust is the normal discriminator. For the zinc alloys, TCP appears to perform slightly better than chromate. For the IVD aluminum and Alumiplate, each post treatment performed about the same. Activating the aluminum coatings appears to incrementally improve the corrosion performance of TCP. Activation is not normally done in a production environment where fresh coatings are processed in a rapid sequence that minimizes oxide formation on the metallic coatings. NAVAIR is unable to produce all of these coatings in house so a compromise is necessary to gain high quality, commercial-representative coatings. Future testing will incorporate TCP in the direct production sequence and compare performance to delayed TCP coating and re-activation.

Figure 6: Alumiplate with chromate (R) and TCP (L) after 1000 hours of ASTM B 117 salt fog

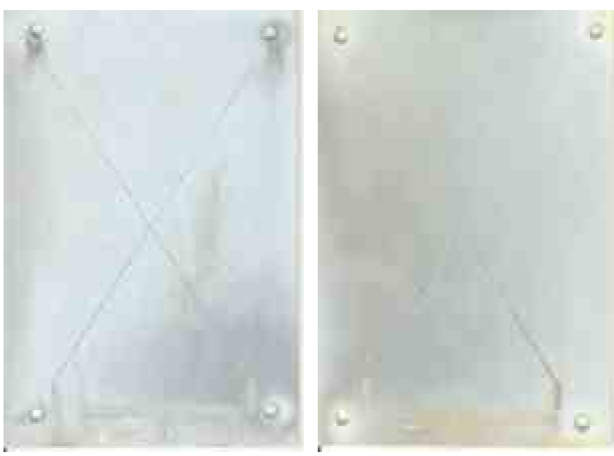
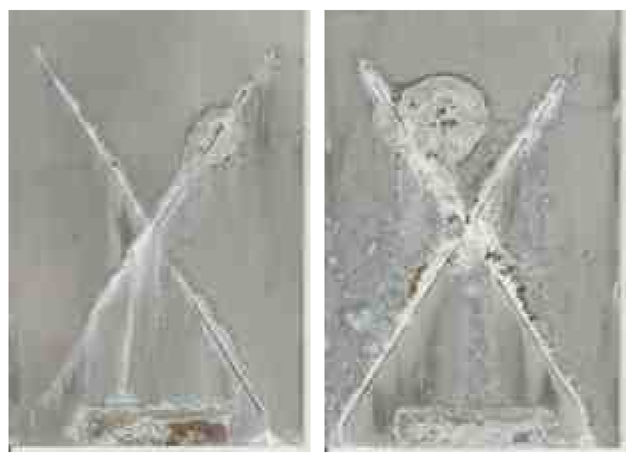


Figure 7: IVD Al with chromate (R) and TCP (L) after 1000 hours of ASTM B 117 salt fog



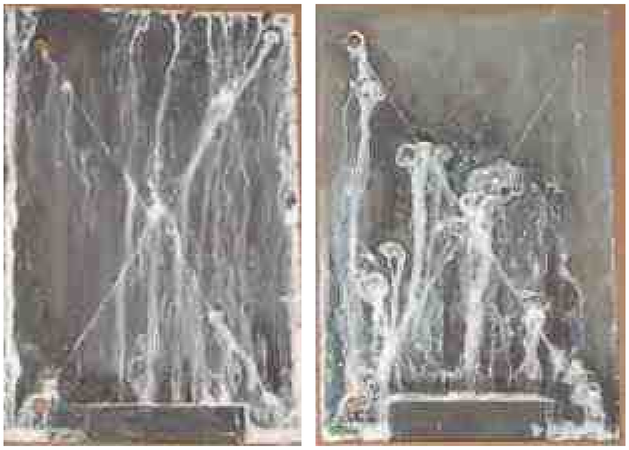


Figure 8: Boeing Zn-Ni with chromate (R) and TCP (L) after 1000 hours of ASTM B 117 salt fog

Figure 9: Dipsol Gumm Zn-Ni with chromate (R) and TCP (L) after 1000 hours of ASTM B 117 salt fog

Figure 10: Tin-Zinc with chromate (R) and TCP (L) after 1000 hours of ASTM B 117 salt fog

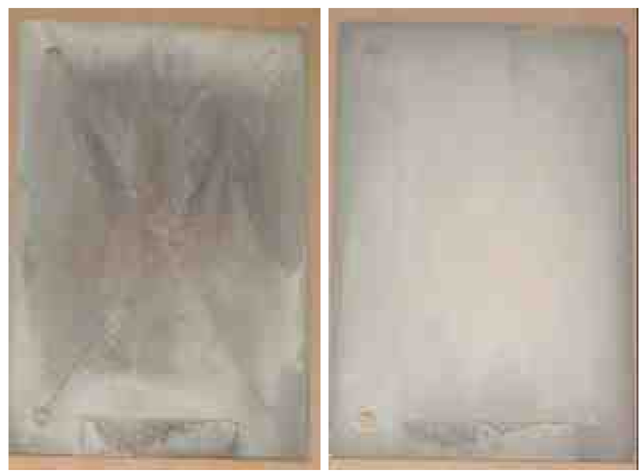


Figure 11: Cadmium with chromate (R) and TCP (L) after 1000 hours of ASTM B 117 salt fog

A caution is in order not to generalize overall performance here since salt fog tests are known to be variable. Importantly, though, the overall performance trend of TCP shows that it is about as good as chromates for this initial evaluation. Interestingly, TCP works universally on three different metal systems: cadmium, aluminum and zinc. Other post treatments and their processes are specific to each metal, or even for a specific alloy. This is a process advantage to post treating mixed metal systems during repair of components where currently each alternative needs to be post treated with its unique chemical.

Experiment 2

The Department of Defense is funding a project at the National Defense Center for Environmental Excellence to evaluate the performance of a modified IVD aluminum process coupled with non-chromate post treatments. IVD aluminum was deposited on 4130 steel coupons. The goal of the project is to identify an optimum process that does not require burnishing and uses a chromate-free post treatment[8].

NAVAIR participated in the project by post treating various types of IVD aluminum with three different TCP processes. Processing was done on site immediately after IVD aluminum processing and no re-activation was used. Table 3 details the coatings produced.

Table 3: IVD Al coating and Post Treatment Variables

Coating	Peened/Burnished	Post Treatment
Conventional IVD	Yes	None, Alodine 1200S (control), TCP w/5 min immersion, TCP w/10 min immersion, TCP w/color change (10 min immersion)
	No	None, Alodine 1200S (control), TCP w/10 min immersion, TCP w/color change (10 min immersion)
Modified IVD	Yes	None, Alodine 1200S (control), TCP w/5 min immersion, TCP w/10 min immersion, TCP w/color change (10 min immersion)
	No	None, Alodine 1200S (control), TCP w/10 min immersion, TCP w/color change (10 min immersion)

For this test, the TCP described in Experiment 1 was used, as well as a newer version developed to enhance the color change of TCP on aluminum coatings. Figures 12 through 17 detail the appearance of chromate, TCP and TCP with color change additive on standard and modified, peened and unpeened, IVD aluminum. The minimum allowable thickness of IVD aluminum was targeted: 0.3 mils, or 0.0003 inches thick. Table 4 shows that most coatings fell into the 0.3 to 0.5 mil thickness range.

For evaluation of corrosion performance, unscribed coatings were exposed to ASTM B 117 neutral salt fog. Performance was determined by visual analysis of coupons at prescribed intervals, noting the initial appearance of red rust through the coating. The appearance of red rust on the test coatings is shown in Table 5. Four test coupons were tested for each coating system. In the table these are noted randomly for each coating with the worst performing test coupon appearing on the left. The numbers in the table note the time range when red rust appeared.

Figure 12: Conventional IVD Al with chromate control

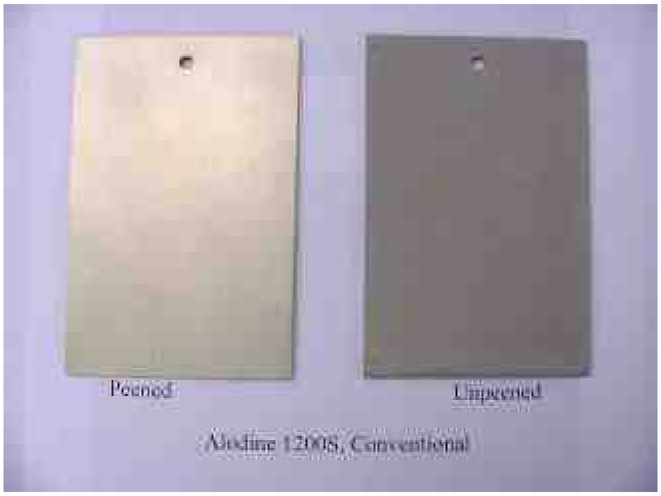


Figure 13: Conventional IVD Al, peened, with 5 and 10 min TCP

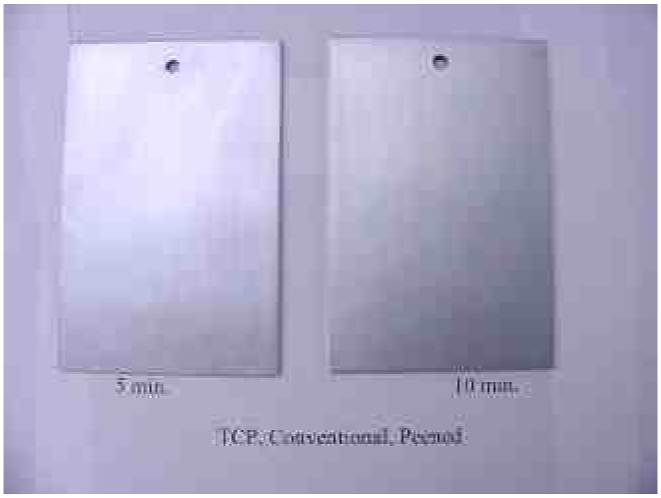


Figure 14: Modified IVD Al, peened, with 5 and 10 min TCP

Figure 15: Conventional IVD Al, peened, comparing TCP to TCP with color change

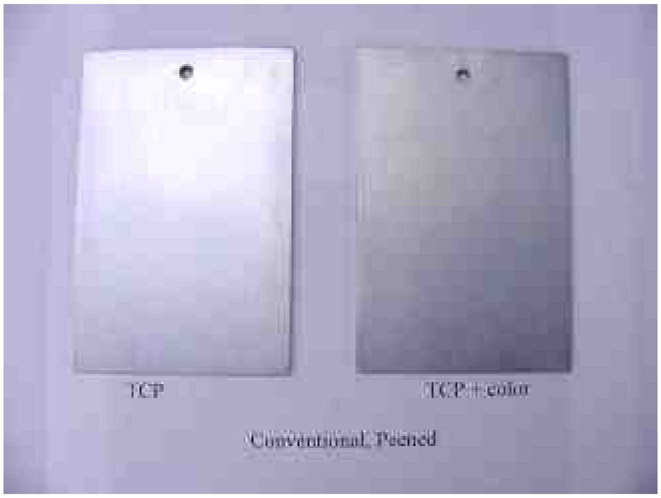


Figure 16: Conventional IVD Al, unpeened, comparing TCP to TCP with color change

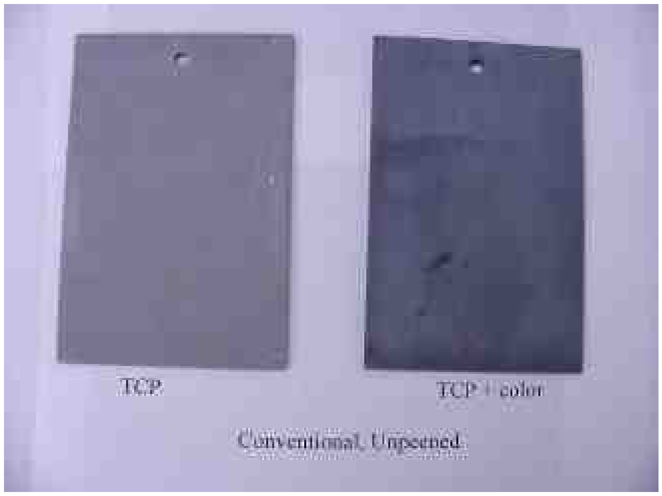


Figure 17: Modified IVD Al, peened, comparing TCP to TCP with color change

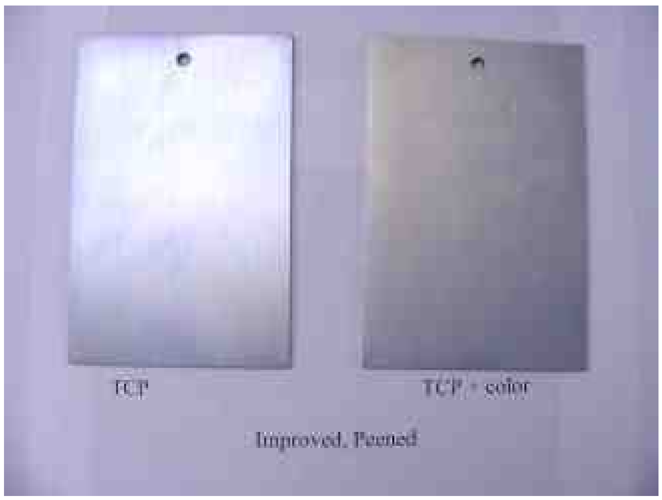


Table 4: Ion Vapor Deposited Aluminum on 4130 Steel-
Coating Thicknesses of IVD Aluminum After Processing with Various Post Treatments

IVD Type	Post Treatment Scenario		Thickness (mil)	
	Glass Bead Peen	**Conversion Coating**	**Calculated**	**Fractured**
Conventional	X	None	0.51	0.47
			0.55	
Conventional		None	0.51	0.55
			0.47	
Conventional	X	Alodine 1200S	0.51	0.51
			0.55	
Conventional		Alodine 1200S	0.55	0.51
			0.51	
Conventional	X	TCP - 10 min	0.55	
			0.55	0.51
Conventional		TCP – 10 min	0.51	
			0.51	

IVD Type	Post Treatment Scenario		Thickness (mil)	
	Glass Bead Peen	Conversion Coating	Calculated	Fractured
Conventional	X	TCP - 5 min	0.55	
			0.55	
Conventional	X	TCP w/color change– 10 min	0.47	
			0.55	
Conventional		TCP w/color change– 10 min	0.55	
			0.51	
Improved	X	None	0.55	0.49
			0.51	
Improved		None	0.43	0.55
			0.47	
Improved	X	Alodine 1200S	0.55	
			0.43	0.39
Improved		Alodine 1200S	0.39	0.45
			0.39	
			0.47	0.55
Improved	X	TCP – 10 min	0.45	
			0.39	0.43
Improved		TCP – 10 min	0.43	
			0.39	0.39
Improved	X	TCP – 5 min	0.51	
			0.59	
Improved	X	TCP w/color change– 10 min	0.43	
			0.38	
Improved		TCP w/color change– 10 min	0.38	
			0.55	

Table 5: Ion Vapor Deposited Aluminum on 4130 Steel- Corrosion Performance of IVD Aluminum After Processing with Various Post Treatments (Hours to Red Rust while Exposed to ASTM B 117 Neutral Salt Fog)

IVD Treatment	Post Treatment Scenario		First Signs of Red Rust (hours) Note: onset of rust in time range listed			
	Glass Bead Peen	Conversion Coating	Coupon 1	Coupon 2	Coupon 3	Coupon 4
Conventional	**X**	None	288-336	336-384	336-384	336-384
Conventional		None	384-432	600-672	600-672	672-720
Conventional	**X**	Alodine 1200S	432-552	672-720	840-888	888-936
Conventional		Alodine 1200S	552-600	672-720	840-888	840-888
Conventional	**X**	TCP-10 min	552-600	552-600	768-840	1200-1248
Conventional		TCP-10 min	768-840	888-936	936-1008	936-1008
Conventional	**X**	TCP-5 min	384-432	432-552	432-552	432-552
Conventional	**X**	TCP w/color change-10 min	672-720	1056-1104	2016-2112	2184-2280
Conventional		TCP w/color change-10 min	840-888	1440-1560	2016-2112	2280-2376
Improved	**X**	None	216-288	216-288	216-288	216-288
Improved		None	336-384	336-384	336-384	432-552

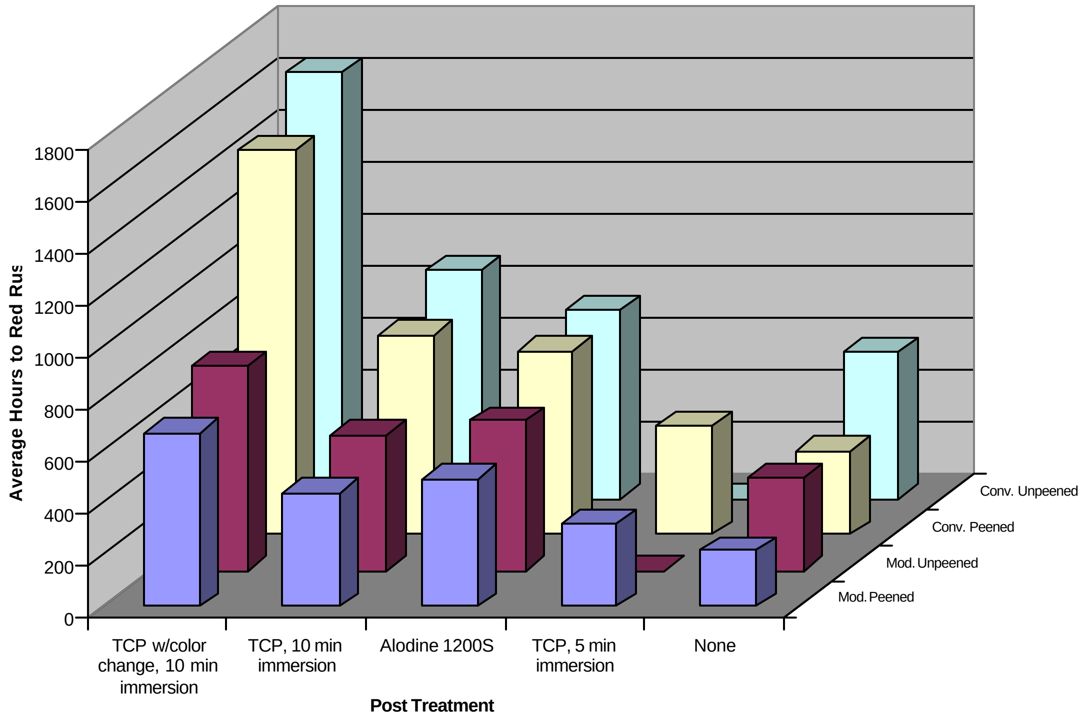
IVD Treatment	Post Treatment Scenario		First Signs of Red Rust (hours) Note: onset of rust in time range listed			
	Glass Bead Peen	**Conversion Coating**	**Coupon 1**	**Coupon 2**	**Coupon 3**	**Coupon 4**
Improved	X	Alodine 1200S	384-432	432-552	552-600	600-672
Improved		Alodine 1200S	384-432	432-552	600-672	888-936
Improved	X	TCP-10 min	264-336	384-432	432-552	672-720
Improved		TCP-10 min	432-552	552-600	552-600	552-600
Improved	X	TCP-5 min	264-336	336-384	336-384	336-384
Improved	X	TCP w/color change-10 min	432-552	600-672	600-672	1056-1104
Improved		TCP w/color change-10 min	720-768	720-768	888-936	840-888

Based on the average onset of red rust, TCP with color change additive surpassed all other coatings in performance regardless of IVD aluminum process type or peening, in some cases by as much as 100 percent. Baseline TCP applied with a 10-minute immersion was similar to the chromate post treatment. The TCP applied for 5 minutes was better than no post treatment, but not as good as the chromate or other TCP coatings. Table 6 and Figure 18 detail the average onset of corrosion for each TCP coating compared to the chromate control.

Table 6: Average Onset of Red Rust for Post Treatments on IVD Al

Coating	Post Treatment	Average Onset of Red Rust, hours	
		Peened	**Unpeened**
Conventional IVD	None	324	564
	Alodine 1200S	708	726
	TCP, 5 min immersion	420	NA
	TCP, 10 min immersion	768	882
	TCP w/color change, 10 min immersion	1482	1644
Modified IVD	None	216	360
	Alodine 1200S	492	576
	TCP, 5 min immersion	318	NA
	TCP, 10 min immersion	438	522
	TCP w/color change, 10 min immersion	672	792

Figure 18: Average Onset of Red Rust for Post Treatments on IVD Al



Summary and Plans

TCP coatings used as post treatments for sacrificial coatings show equivalent or better corrosion performance in salt fog tests compared to chromate post treatments. An improvement to TCP, originally designed to impart practical color change to sacrificial coatings, yields coatings with better corrosion performance than chromate controls in unscribed salt fog testing.

Additional work is underway to optimize the TCP and TCP plus color change processes, as well as validate their performance on various thicknesses of IVD aluminum coatings. TCP and TCP plus color change processes will also be evaluated and optimized for other sacrificial coatings, including zinc, zinc-nickel, tin-zinc and cadmium. Planned tests include scribed and unscribed neutral salt fog, SO_2 salt fog, cyclic corrosion, outdoor exposure, and paint adhesion.

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