NON-PHOSPHATE TRANSITION METAL COATINGS

BY BRUCE DUNHAM AND DR. DAVID CHALK, DUBOIS CHEMICALS, SHARONVILLE, OHIO

INTRODUCTION

Traditional iron phosphate and zinc phosphate conversion coatings have been used for more than a century as pretreatments for painting over a variety of metals. These "legacy" phosphate pretreatments have served well; however, environmental regulations restricting phosphate discharge, increased phosphate and zinc costs, and higher corrosion-resistance requirements have provided impetus for the development of non-phosphate alternatives. During the evaluations of the various technologies, it was discovered that these new non-phosphate pretreatment conversion coatings conferred significant cost savings and operational benefits along with their promised decreased environmental impact.

Considered new and experimental in the New Millennium (Y2K), these non-phosphate conversion coatings have gained significant traction in the pretreatment market and are rapidly becoming the technology of choice for paint and powder coating pretreatment. The purposes of this article are to provide background information for those new to non-phosphate pretreatments, and to answer some frequently asked questions about the non-phosphate conversion coatings.

WHAT ARE TRANSITION METAL COATINGS?

If iron phosphate and zinc phosphate can be referenced as "Traditional Metal Phosphates", the new non-phosphorus pretreatments can rightly be called "Transition Metal Coatings" (and will be referenced as "TMC" coatings in the remainder of this paper).

The term "transition metal" refers to a metal's position in the Periodic Table of the Elements, and is a term chemists use to describe the location of a group on the Table.

Zirconium (Zr) is at the center of a group of elements in the Periodic Table that are considered relatively environmentally friendly. (See Figure 1) Oxides of zirconium, titanium, and/or vanadium are the most commonly used transition metal coatings, with zirconium as the most frequently encountered transition metal. Note the location of these metals relative to chromium. The closer two given elements are to each other on the Periodic Table, the more similar their properties.

The first recorded application of zirconium oxide on steel was in 1996, when the first non-chrome seal rinse based on zirconium was introduced. Applied over a traditional metal phosphate conversion coating, the sealer conferred corrosion resistance that was close to that offered by the chromium seal rinse that had traditionally been used.

The chemistry was then modified in 1998 to serve as a chromium replacement for conversion coating on aluminum. The first applications for steel arrived in 2002.

WHAT IS THE APPEARANCE OF A TRANSITION METAL COATING PRETREATMENT?

Zirconium oxide is a very versatile material, taking on such varied forms as

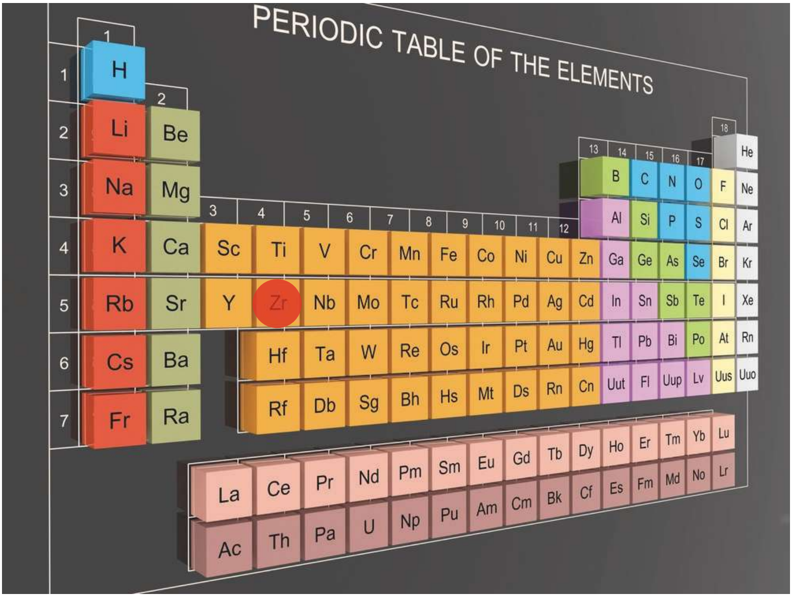

Figure 1. Periodic Table of Elements—note Zirconium's position.

ceramic bake ware, or when fused as jewelry, cubic zirconia. Imagine cladding a reactive metal in an inert substance like cubic zirconia, then applying a corrosion-resistant organic coating. This is the promise of the modern transition metal coatings, once referenced as nano-ceramic.

Figure 2 shows the relative thicknesses of the pretreatments. When gauging relative thickness of applied pretreatments, zinc phosphates are by far the heaviest and thickest pretreatments, depositing a mineral layer of some 1000 to 5000 nanometers (nm) in thickness. (Footnote 1) Iron phosphate applies typically a 250 to 500 nm thick coating. TMC pretreatments are approximately 50 nm, with some approaching 200 nm in thickness. They are the smallest, thinnest of the pretreatments, and are much thinner than the traditional metal phosphates they replace.

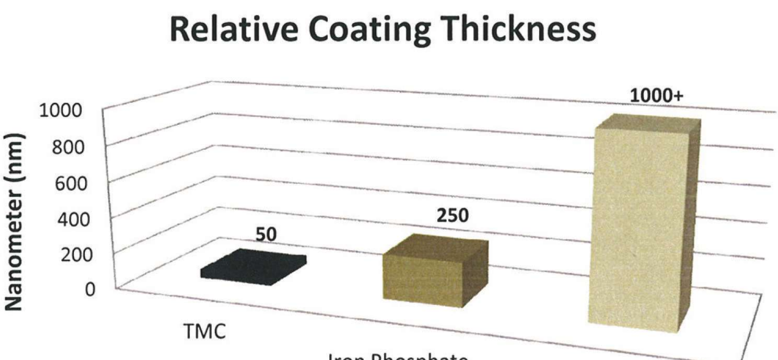

Figure 2. Relative coating thickness of transitional metal coatings, iron phosphate and zinc phosphate.

Figure 2a. Pretreatment comparison.

	TMC*	Iron Phosphate	Zinc Phosphate
Coating Structure	Amorphous	Amorphous	Crystalline
Typical Coating Thickness	~50 nm	~250 nm	1000 nm
Typical Coating Weight	50-150 mg^2 5-15 mg/ft^2	300-700 mg/m^2 25-65 mg/ft^2	2-3 g/m^2 180-300 mg/ft^2
*TMC = Transitional Metal Coating			

Much like traditional phosphates, TMC pretreatments can exhibit an array of colors, from nearly colorless, to tan, gold, and iridescent blue. Investigation has revealed that the appearance of pretreated metal is related to the thickness of applied coating. When the substrate is mild steel, the coating color goes from the original appearance of the substrate to light gold or tan, to a deep gold, to light blue and gold, to blue, to deep iridescent blue as the coating becomes more complete and increases in coating weight or thickness. As with traditional phosphates, the coating will become higher with increases in one or more of the following variables: chemical concentration, contact time, pressure (spray) or agitation (immersion), or temperature.

Another significant variable that impacts appearance of the coating is the type of steel a finished good is made from and the fabrication steps required to produce it. Heat treatment, welding, grinding, bending, blasting and other common manufacturing processes impact the amount of carbon (or scale) and iron at the surface of the part. The more carbon at the surface, the less reactive the surface is to the pretreatment solution. The more iron at the surface, the more reactive the surface is to the pretreatment solution. The photos below show a mild steel and hot rolled steel panel. Both panels were processed through a five-stage pretreatment process (Clean, Rinse, TMC, Rinse, Final Seal). The cold rolled steel is an even deep blue and the hot rolled steel is an even grey color because of the high carbon content at its surface.

WHAT ARE THE BENEFITS OF REPLACING PHOSPHATE CONVERSION PRETREATMENTS?

The primary benefit of replacing traditional metal phosphate pretreatments is significant and measurable cost savings in the operation/application of TMC pretreatments.

A significant benefit of replacing traditional metal phosphate with TMC pretreatments is the elimination of phosphorus from the waste stream. Phosphorus is becoming increasingly regulated, especially in areas near large bodies of fresh water such as the Great Lakes region; watersheds such as the Chesapeake Bay; and other areas where municipalities are trying to reduce phosphates in the water they discharge back into the environment. Minimizing

Footnote 1 - Note that a nanometer is on one billionth of a meter so the "smallness" of the concept is difficult to grasp. Put more succinctly, a nanometer is to a meter, what a marble is to the earth.

phosphates in water is a strategy aimed at reducing eutrophication (Footnote 2). Adopters of TMC pretreatments often claim a green pretreatment strategy; the disposal procedures are generally inexpensive and uncomplicated.

TMC pretreatments are very reactive so heat is not needed to drive the reaction of the zirconium with the metal at the surface of the part. Thus, TMC pretreatments can run at ambient temperature, whereas the traditional metal phosphates require significant heat to drive the deposition reaction. This saves significant energy cost.

Most TMC pretreatments operate between 90 and 105°F. The heat carried in by the parts coming from the heated cleaner stage and the energy generated by the pump in a spray system are typically enough to maintain this temperature range.

Early adopters of TMC pretreatment technology enjoyed a minimum of 15%, to as much as 40% lower costs when converting from traditional metal phosphate pretreatments. These kinds of savings persist with the modern renditions of TMC pretreatments.

Figure 3 Top: Heavy zirconium oxide coating on hot rolled steel. Bottom: Heavy zirconium oxide coating on cold rolled steel.

Another key benefit of TMC pretreatments is much better corrosion performance in service, as well as in accelerated testing, when compared to the legacy metal phosphates (10% to 30% longer salt spray hours and more intervals of cyclic corrosion testing have been observed with the first versions of this new class of chemistry). Several suppliers of pretreatment chemistry have developed TMC pretreatments that are approaching the performance of zinc phosphate. Because of high operational and disposal costs associated with running a successful zinc phosphate process, OEM's are investigating substituting TMC for zinc phosphate pretreatment, and several organizations have successfully made the transition.

There are several reasons why TMC pretreatments provide excellent corrosion protection. As previously noted, TMC contain elements that are near chromium on the period table; the oxides of these elements are relatively chemically inert so they do not dissolve as easily as phosphate metal coatings. Zirconium oxides are so stable that hydrofluoric acid, which is extremely corrosive and aggressive, is needed to dissolve them. Secondly, TMC are made of much smaller particles than amorphous iron phosphate coatings or zinc phosphate crystals. Because the par-

Footnote 2: Eutrophication: or more precisely hypertrophication, is the ecosystem response to the addition of artificial or natural substances, such as nitrates and phosphates, through fertilizers or wastewater, to an aquatic system.

ticles are so small, they are able to pack closer together. This results in less void space within the matrix of the TMC when compared to conventional phosphate metal coatings, so there is less room for air, moisture, and salts to travel to the substrate and cause corrosion. These coatings also inhibit galvanic corrosion because the transition metal has electrons that would be sacrificed prior to the electrons of the iron in the base metal.

Paint/powder coating adhesion and corrosion resistance also benefit because of the efficiency of the reaction. As stated, the efficient reaction results in very little sludge formation, so there is much less suspended solids in the pretreatment solution. As the pretreatment bath ages and the level of insoluble suspended solids increases, they can become incorporated in the phosphate coatings and/or dry down on top of them despite rinsing. The result is a powdery appearance on the parts that provides an inferior surface for adequate paint or powder coating adhesion. If you have managed an iron or zinc phosphate pretreatment process, you have likely made the decision to dump the bath at the end of its useful life due to powdery part appearance in your past.

The reader may be thinking, "If it saves costs, increases environmental compliance, and gives better performance, what's not to like?" The market agrees, and adoption of TMC pretreatments is therefore rapidly increasing in the marketplace.

HOW ARE TRANSITION METAL COATINGS DIFFERENT (FROM TRADITIONAL PHOSPHATE)?

New users observe several differences when converting from the legacy phosphate pretreatments.

- **TMC are best applied at cool temperatures, not warm-to-hot like phosphate.**
- **TMC are MUCH more reactive than phosphates during application, yet they sludge much less. They benefit from a continuous filtering regimen to remove iron solids.**
- **TMC can be (and are) used in mild steel washers, but are best applied from stainless equipment.**
- **TMC are equally as well applied via spray, immersion, and pressure wand.**
- **TMC require excellent rinsing and low-salt content applications along with a very clean surface.**

HOW ARE TRANSITION METAL COATINGS THE SAME (AS A PHOSPHATE)?

New users of TMC pretreatments are delighted to find that there are many similarities with the traditional metal phosphates.

- **TMC pretreatments are usually applied from a washer and generally will change the color of the metal substrate (if it's steel). The color change can give a good visual indication of a properly running process.**
- **The application mechanism of TMC pretreatments is somewhat similar to phosphate, with pickling of metal and depositing of coating. There is a bit of a difference in that the substrate metal is not generally believed to be a participant in the deposition reaction**

Table 1. Five-Stage TMC Sytem

Process Stage						
	1	2	3	4	5	**Comments**
Option 1	Clean	Rinse	TMC	Rinse	Seal	Legacy Iron Conversion
Option 2	Clean	Rinse	Rinse	TMC	Rinse/Seal	New TMC Line Design
Option 3	Clean/TMC	Clean/TMC	Rinse	Seal	Rinse/Seal	Clean-Coater TMC

mechanism.

- **The application requires some measure of control and attention to the process. Typical measurements are for pH, acidity, and perhaps a colorimeter to measure the transition metal concentration.**
- **TMC pretreatments work by passivating the substrate with respect to corrosion, and enhancing mechanical/physical paint bonding— the same as traditional pretreatments.**

CONVERTING FROM PHOSPHATE TO TMC

There are generally two types of conversions: the washer is an existing traditional metal phosphate application, or the washer is newly constructed for application of TMC pretreatments. The two applications require different approaches.

A legacy metal phosphate washer will typically feature a cleaning stage, one rinse, a pretreatment application stage, one or more rinses and perhaps a seal rinse.

The best practice for TMC is stainless steel for the TMC stage, good cleaning, very good rinsing, and perhaps provision for a seal rinse. At first glance it would be considered fairly straightforward to simply replace the traditional metal phosphate stage with a TMC stage. Unfortunately, this overlooks the need for very thorough rinsing ahead of the TMC stage. More frequently, a conversion of the legacy metal phosphate stage to a rinse, followed by conversion of a legacy rinse to a TMC stage is more successful. New washer construction takes into account the requirement of sufficient rinsing ahead of pretreatment by inserting an extra rinse after cleaning.

Three-stage washer configurations present a particular challenge because the process must both clean the metal and provide a conversion coating. Surfactants cannot be incorporated into zinc phosphate baths so the cleaning and pretreatment must be in separate stages, separated by a minimum of 1 rinse. Zinc phosphate requires a minimum of 5 stages and more typically 7 stages. Iron phosphate is commonly applied in a three-stage process, where the cleaning and conversion coating is accomplished in the first stage. The cleaning is achieved the addition of both the surfactant and/ or solvent into the formula. When parts are heavily soiled with mill oils and other metalworking fluids, it is not uncommon to use a tank side additive to improve cleaning and extend the useful life of the bath.

As previously stated, TMC do not contain phosphate. While this is an environmental benefit, it diminishes the cleaning capability of the chemistry because phosphates are a detergent and help cleaning. TMC must rely solely on surfactants and solvents in the formula to degrease the metal. cleaner-coater TMC products are available and are best used when the soil load is light and consistent.

Table II. Three-Stage TMC System

Process Stage				
	1	2	3	Comments
Option 1	Clean	Rinse	TMC	For dry-in-place time TMC
Option 2	Clear/TMC	Rinse	Rinse/Optional Seal	Clean-coater TMC

Table III. Three-Stage Spray Application Methods

	Stage One	Stage Two	Stage Three
Process	Clean	Rinse	TMC (Dry-In-Place)
Time	90 sec	30-45 sec	45-60 sec
Temperature	95-130°F	Ambient	Ambient
Concentration	2%-4%	n/a	2%-4%
pH	Alkaline	Neutral	Acidic

The most common way of using TMC in three-stage pretreatment processes is to apply them in the final stage. The clean, rinse, coat configuration is ideal for manufacturers that have tough to remove soils and inconsistent sources of steel. A custom coater with 3-stage washer is a good example of an organization that could benefit.

Users of these technologies report varying degrees of satisfaction, but with creative use of vestibule space for misting risers to provide better rinsing, and good chemical product selection, a 3-stage washer can give satisfactory service. The 5-stage washer configuration will give much more flexibility in the application of TMC pretreatments.

Of particular interest are conversions of legacy zinc phosphate systems to TMC pretreatments. With performance of TMC pretreatments approaching that of zinc phosphate, without the detriments of heavy sludge, high process cost, and need for onsite waste water treatment, these old washers are being converted with increasing frequency. The most important consideration is the removal by acidic descaling of the old sludge and activator products from the washer surfaces. Using a hot recirculating solution of muriatic acid will dissolve old zinc phosphate scale, corrosion products, titanium salts, and other deposits, leaving the washer ready to accept the new TMC pretreatment. Failure to descale the washer will cause contamination and compromise performance of the new pretreatment.

CONCLUSION

TMC are now widely used across the globe by hundreds of users in a broad range of industries. This technology is the fastest growing powder coating and paint pretreatment and is firmly established in the finishing market. It is no longer considered “new”. The technical support to convert existing metal phosphate pretreatment systems is well established. The newest TMC products are easy to run, so there are no barriers to enjoying the benefits to your process offered by TMC. If you are interested in improving the corrosion resistance of your product and the environmental profile of your pretreatment program, you may consider TMC.