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Zirconium Pretreatments: Not Just for Early Adopters Anymore

Abstract. Zirconium oxide conversion coatings have proven to be excellent replacements for iron phosphate pretreatments in recent years. The substantial performance, operational, and environmental benefits have been well documented. "In the past two years of testing, less than 5% of results favor an iron phosphate over Zirconization or other non-phosphate technology," said David Schimpff, DuBois Chemical's Business Sector Leader.

Many chemical suppliers, including DuBois Chemicals, have dedicated significant resources to developing modern Zirconization™ options that address the early weaknesses exhibited by this underutilized technology. Despite the many advantages—such as reduced energy consumption, phosphate-free processes, low sludge, and high salt-spray performance—the majority of finishing operations continue to use iron phosphate. Is this because the "technology is too new?" Maybe you have heard about an installation that didn't go smoothly? Quite possibly, you may perceive iron phosphate as more forgiving and easier to use?

This article addresses some frequently asked questions regarding zirconium pretreatments and shares some benefits of the most recent generation of the technology.

What are the key differences between conventional pretreatment and Zirconization?. Conventional phosphate-based pretreatments (i.e., iron phosphate and zinc phosphate) have been the primary conversion coating of choice for about 100 years. With Zirconization, zirconium oxide replaces the iron phosphate in the conversion coating. There are several reasons why this is beneficial. First, phosphorus is becoming more restricted because it supports algae growth in ponds, lakes, and other waterways. The excess algae growth contributes to eutrophication[1]. A second environmental benefit is the reduced demand for process heating; the zirconium pretreatments do not require heating, so they are more cost effective to operate than processes that require 100–160°F. Finally, the zirconium oxide conversion coating provides excellent corrosion resistance properties to steel and aluminum.

How long has zirconium been used in metal pretreatment? The very first application of zirconium on steel was developed as a chromium-free final rinse replacement in the mid-1990's by Dr. David Chalk, a chemist for Texo at the time. While the new chemistry gave excellent salt spray[2] results in a laboratory setting, there were application problems very similar to the some of the first experienced with the early zirconium pretreatments.

In 1998, Fremont Industries discovered that zirconium-based conversion coatings for aluminum gave excellent corrosion performance. (They began to replace hexavalent chromium for that application.) In 2002, the concept of applying zirconium as a pretreatment on steel, as opposed to a sealer, was introduced to the market by Henkel. Several other suppliers quickly followed into the marketplace.

These very early efforts to commercialize the zirconium technology as a pretreatment encountered significant application problems that have since been resolved. For example, the application problems included steel that would rust very quickly before it could even be dried off.

The early zirconium oxide conversion coatings relied solely on strong acids to activate the surface of the metal and drive the reaction. Nitric acid was (and is) commonly used by many suppliers of Zirconium-based pretreatments. The dependence on nitric acid aggravates in-process rust problems with industrial application of zirconium oxide coatings.

Low bath life was also a characteristic of the early versions of these materials. One of the best ways to measure bath efficiency is to evaluate bath life and sludge generation. Almost every operating phosphate bath will be opaque in some way. Depending on the accelerator[3] used, iron phosphate will build sludge, which comprises un-deposited iron phosphate, iron oxides, and hard

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[1] *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 sewage, to an aquatic system.*

[2] *Accelerated Corrosion Test*

[3] *An important ingredient in metal treatment products that allow the coating reaction to start and occur at low chemical concentrations and temperature.*

	Iron Phosphate	Zinc Phosphate	Zirconization™
Corrosion Resistance (ASTM B-117 NSS)			
CRS	Standard	Excellent	Excellent
HRS	Standard	Excellent	Good
Cast Iron	Standard	Excellent	Good
Galvanized	Standard	Excellent	Good
Aluminum	Standard	Good	Excellent
Adhesion			
HRS Pickled/Oiled	Standard	Excellent	Good
Cross Hatch	Good	Good	Good
Impact Resistance	Good	Poor	Excellent
Operational Considerations			
Total Operational Cost	Standard	Poor	Excellent
Ease of Use	Excellent	Not Recommended	Excellent
Ambient Temp Operations	Good	Poor	Excellent
Nozzle Maintenance	Standard	Poor	Excellent
Sludge for Volume	Poor	Poor	Excellent
Safe for Mild Steel	Good	Poor	Good
Safe for Stainless Steel	Excellent	Excellent	Excellent
Environmental Impact			
Energy Savings	Standard	Poor	Excellent
Phosphate Free	Not Recommended	Not Recommended	Good
Ease of Waste Treatment	Excellent	Poor	Excellent
Application			
Pressure Wand	Excellent	Not Recommended	Excellent
Immersion	Excellent	Excellent	Excellent
Spray	Excellent	Excellent	Excellent
3 Stage	Excellent	Not Recommended	Good
5 Stage	Excellent	Good	Excellent

KEY

- Excellent
- Good
- Standard
- Poor
- Not Recommended

water salts. As the sludge (white or tan in color) builds, it drops to the bottom of the tank and fouls heat exchange surfaces and plumbing, thereby reducing heat transfer efficiency. A zinc phosphate bath is often choked with sludge that includes both un-deposited zinc phosphate and excess iron that dissolved from the work pieces. In sharp contrast to phosphate conversion coatings, almost all of the reaction products in a Zirconization process are soluble salts.

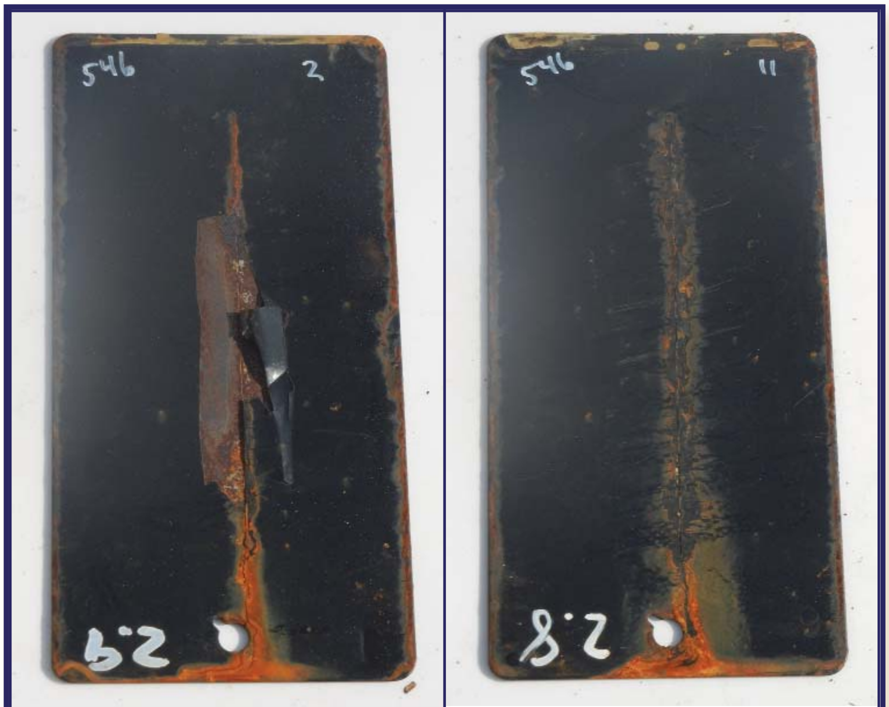

Figure 1 (top). Pictured are samples of test panels from some of the many experiments when developing the Zirconization chemistry. The powder coating used is rated for 500 hours neutral salt spray (NSS) with an iron phosphate/non-chrome final rinse. The Standard Zirconium (left) failed at 576 hours NSS, whereas the new technology (right) passed at 1000 hours NSS.

Figure 2 (bottom). The main attributes of Zirconization are its ease of use and fast coating capability. The mild steel panel on the left (gold) was treated with a standard zirconium product, while the panel on the right (blue) was treated with new technology/Next Generation Zirconization. The coating is heavier and more complete, which is exhibited by the darker blue color.

THE NEXT GENERATION

Next-generation Zirconization addresses the key challenges common to most non-phosphate metal preparation programs. While increased paint adhesion and corrosion resistance are features of the most recent technologies, the most popular attributes are related to ease of use.

Easy to Start-Up & Maintain Bath. Most iron, zinc, and phosphate-free pretreatment baths require significant adjustment procedures and/or bath break-in periods to avoid flash rust upon start-up. The next-generation products minimize and often eliminate the need to make any pH adjustment prior to running production. The new generation products are also easier to maintain on a day-to-day basis because the conversion coating reaction is more stable and pH swings are eliminated. Because there are fewer adjustments, there is much less salt building in the bath to upset operation and generate sludge—which results in a much longer bath life.

Faster and complete coating. The technology enables a corrosion-resistant zirconium oxide coating to be formed faster than ever before. The result is a more intense color change of the steel surface that is easier to see (Figure 2).

<u>Speed of Coating:</u> In an industrial setting , variable soil load and dense part racking practice all but guarantees that the coating will form more easily on some areas than others. Areas of the parts that are dirtier

and/or racked further from the nozzles will form their coating after clean metal areas racked closer to the impingement of the spray nozzles. Light and inferior coatings could be formed in some cases. The increased rate of reaction maximizes the probability that a sufficient zirconium oxide coating is formed. The new technology is capable of forming a coating with minimal contact time (approximately 30 seconds) at ambient temperatures.

Complete Color Change: When zirconium oxide coatings form on steel, the color transitions from gold to blue (see Figure 2) with increased exposure (time, temperature, and/or concentration). Most early generation zirconium oxide coatings were gold in color. While the corrosion-resistant functionality of a gold-colored zirconium coating is well established, a negative perception persists in the market. End users confuse gold for flash rust (iron oxide), and in cases where a poor coating is formed, the color can mask the presence of flash rust. The image to the right compares the next generation technology to the current best practice. Note the even blue versus gold coating). Because the new technology coats much faster, the probability of forming a blue coating is greater.

Maximized Coating Adhesion & Salt Spray Resistance. The performance of the new technology consistently exceeds both iron phosphate and other market-leading phosphate-free, zirconium-based metal pretreatment products. The enhanced performance is achieved through the synergy of a uniform, heavier zirconium oxide coating, and the use of proprietary adhesion promoters that "link" the resin in the coating to the metal surface. The coating deposition is complete because we have learned to control the reaction at the surface of the metal to maximize coating formation and minimize the undesirable iron oxide (red rust) side reaction that was so often seen with first-generation products. The accompanying "Pretreatment Performance Summary" (see Table) shows the superiority of the new technology over the legacy phosphate systems.

CONCLUSION

Zirconization, now widely used across the globe by hundreds of users in a broad range of industries, has now become firmly established in the finishing market. It is no longer "new." With the technology now so easy to run, there are no barriers to enjoying the benefits to your process offered by Zirconization. If you are interested in improving the ease of operation, performance, and environmental profile of your metal coating pretreatment program, you may consider Zirconization.

ABOUT THE AUTHOR

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