



# Zirconization™

The Future of Coating Pretreatment

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What is Zirconization? In short, it is a process that utilizes transition metal, low temperature cleaning technology, and rinse water quality maximization techniques. It will enable you to minimize the need for process heat, minimize labor associated phosphate sludge, eliminate phosphates, and maintain or improve quality. It will save you a significant amount of time and money.

The following text is meant to begin your education about the Zirconization Process. The content is the result laboratory work, field testing, and collaborations with end users and co-suppliers.

We will discuss the following topics:

- The current business environment
- The history of phosphate pretreatment chemistries
- Iron vs. Zinc phosphate
- Phosphate alternatives
- The path to Zirconization
- Setting Up and Running a Zirconization Bath
- Zirconization vs. Iron and Zinc Phosphate
- The path ahead

## **Current Business Environment**

It is difficult to pick up a paper or turn on a television without hearing debate over record breaking temperatures, volatile energy prices, global warming, immigration laws, or as some call it, the “Exporting of America”.

The US Census Bureau’s middle-series projections estimate the Nation's population to increase to 392 million by 2050 -- more than a 50 percent increase from the 1990 population size. Some experts believe the our population could grow to as much as 500 million in this time period.

And while there is debate on these issues, most agree that water and energy are precious resources and “Being Green” has become a top priority in many organizations.

Being green is increasingly becoming a requirement to operate competitively, profitably, and legally. A senior manufacturing manager recently stated, “There is no doubt that waste treatment standards are changing, and industries in some communities are facing increases in sewer rates for industrial discharges, which is an additional consideration for reduction or elimination of the waste stream if possible.”

Due to these increasing environmental restrictions and global competition, manufacturing facilities have been forced to consider alternatives to conventional processes. A good example is the European Union. With a population twice as dense as the United States and with fewer freshwater resources, it has, by necessity invoked stringent water regulations. In early 2007, the European Parliament approved legislation that revised regulations on phosphates with a goal of completely phasing them out within three years.

This forced a major shift in the coating pretreatment industry, where best-practice chemistry has traditionally consisted of iron and zinc phosphate treatments.

Consequently, work began on developing non-phosphate based chemistry; specifically in the very challenging area of metal preparation for coating. These efforts have been relatively successful and the base active raw materials of these chemistries are elements from the transition metal group that include Zirconium, Titanium, and Vanadium.

These elements exhibit chemical properties similar to Chrome, but do not have toxicological concerns. As with any new process, there were drawbacks. Most significantly, the requirement for higher water quality, new precision cleaning, and issues associated with flash rusting.

However, recent technological advances have resulted in a new chemistry that addresses these drawbacks, while providing an effective replacement for phosphate chemistries in many pretreatment operations.

This chemical process, known as Zirconization™, not only matches or exceeds the ease of use, paint adhesion, and corrosion resistance provided by typical phosphate-based chemistries, but also provides additional benefits such as less chemical usage and lower operating temperatures.

## **History of Phosphate Pretreatment Chemistries**

Historians refer to the period from 1865-1900 as the Second Industrial Revolution. During this period, advances in the chemical, petroleum, electrical, and steel industries resulted in a new phenomena: the mass production of consumer goods. A need arose to protect these new steel goods from rusting.

British inventor William Alexander Ross provided some of the earliest work on phosphate coatings, filing patents in 1869. In 1906, Thomas Watts Coslett, also from Great Britain, pioneered iron phosphate coatings when he dissolved iron chips into a phosphoric acid bath. Coslett subsequently patented his process in both Great Britain and the United States.

By 1912, inventor Frank Rupert Granville Richards improved upon the Coslett iron phosphate process with the development of a manganese phosphate and this process was patented in 1913. Several improvements were made to the manganese phosphate process over the following twenty years. While this process provided adequate corrosion resistance and paint adhesion capabilities, it required the use of manganese, which was fairly expensive and, with the onset of World War II, difficult to obtain in the United States.

In the 1930s employees of the American Chemical Paint Company developed the zinc phosphate process. This process was more energy efficient than manganese, and became the primary process used on American war materials during World War II.

In the latter half of the twentieth century, improvements were made to iron and zinc phosphate chemistries primarily through the addition of various coating accelerators (organic and inorganic) as well as other additives such as cleaning packages (surfactants and solvents), but the base process and chemistry remained the same.

### **How Do Iron and Zinc Phosphate Compare?**

While manganese phosphate is still used in limited cases, paint pretreatment chemistry today primarily consists of either iron or zinc phosphate. Both have the same goal: to produce a coating on the part which improves paint adhesion and corrosion resistance.

While the goal is the same for each of these chemistries, they produce very different coatings with various strengths and weaknesses. Understanding these relative strengths and weaknesses allow manufacturers to determine which process is best for their operation. You should also have a general understanding to better understand how the Zirconization process can be used to replace either iron or zinc. Iron phosphate produces a non crystalline, amorphous coating on steel substrates.

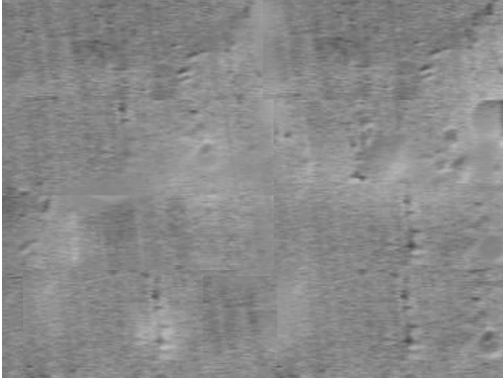


**Figure 1: Steel Q-Panels showing range of possible colors produced by iron phosphate**

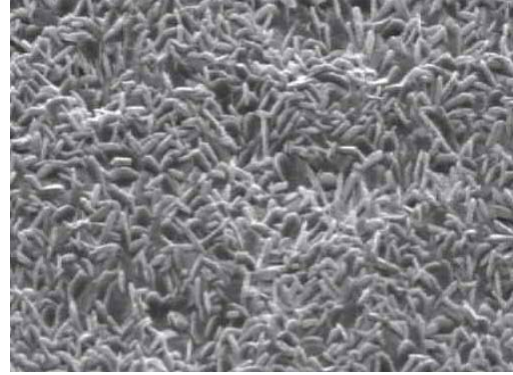
The color of the coating can range anywhere from gray, gold, blue, or purple. It generally produces lower coating weights than zinc, is easy to control, is flexible, robust, and economical.

Iron phosphate processes can be either single or multiple stage processes with cleaning and phosphating occurring in the same stage. Application can be accomplished through spray, soak, wipe, steam, or wand processes. In general, iron phosphate coatings provide excellent physical adhesion and good corrosion resistance.

Zinc phosphate, on the other hand, forms a crystalline coating on parts which is usually gray in appearance. The formation and size of these crystals can be manipulated based on various additives and operating parameters. When compared to iron, zinc phosphate baths produce higher coating weights, are more expensive to run, and are harder to maintain.



**Figure 3: Iron Phosphate Coating**  
SEM Microscopy 1000X



**Figure 2: Zinc Phosphate Coating**  
SEM Microscopy 1000X

Zinc phosphate processes must involve multiple stages and requires a cleaning step and a conditioning step prior to the zinc phosphate stage. Zinc phosphate is applied either by spray or by soak. Zinc phosphate provides good physical adhesion but excellent corrosion resistance.

### **Phosphate Alternatives**

Despite their track record of success over the last century, phosphates have been coming under increasing scrutiny due to their environmental impact on water sources. Simply stated, phosphates cause eutrophication, the increase of chemical nutrients in water that cause excessive plant growth. This plant growth and ultimate decay will lower the oxygen content of water, and result in fish kills due to lack of oxygen.



**Figure 4: Pond showing eutrophication**

Both local sewer districts (MSD's) and the Environmental Protection Agency (EPA) have increasingly forced industries to severely limit, or in some cases, completely eliminate, phosphate discharges, these restrictions are only expected to further increase in the future. If you are lucky enough to not currently face phosphate discharge restrictions, chances are likely that you will be forced to deal with them within the next decade.

In response to the growing concerns over phosphates, chemical suppliers began introducing phosphate-free pretreatment processes to the marketplace. These chemistries included polymeric technology, alternative acids, solvents, primers, and metallic-based coatings. The most popular of these phosphate alternatives has been silane technology.

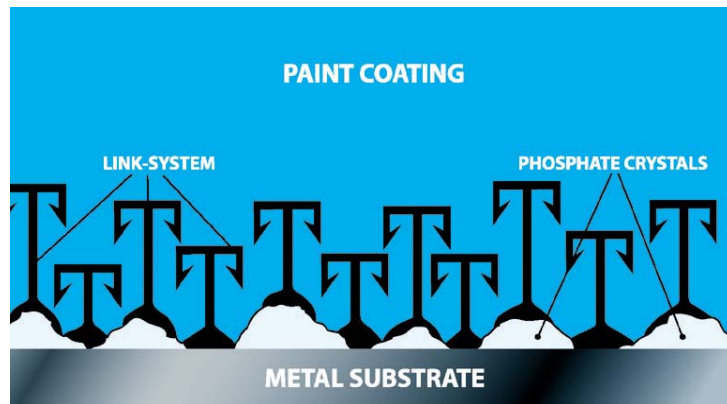


Figure 5: Diagram showing Silane “linking” functionality

Silanes are molecules that have multifunctionality in that one end of the silane will have an affinity for paint, while the other end of the molecule will react with a metal surface. They work for paint pretreatment by ‘linking’ the paint to the metal surface.

While successful in some specific cases, silanes have several disadvantages when compared to phosphates. First, the silane’s reaction with the paint occurs with only certain specific resins so manufacturers who use several different paint resins in the same paint line, typically have had limited success with silane technology.

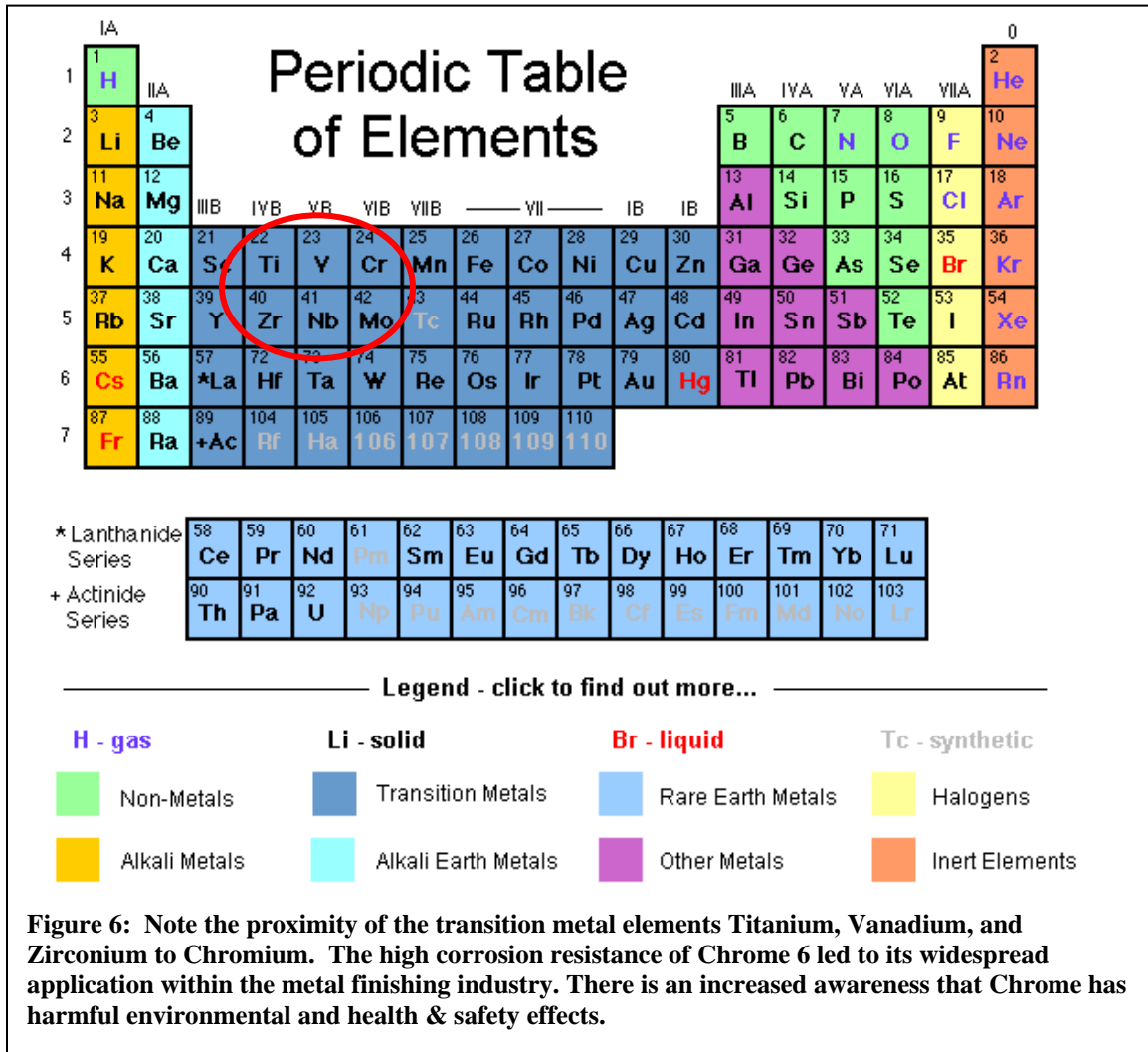
Silanes also are more difficult to control and monitor in tank solutions than iron phosphates. Additionally, silanes are often clear on the part, as opposed to the color produced by phosphate coatings and it is nearly impossible to look at a part and know if the silane coating was properly applied. Silane-treated parts are more susceptible to flash rusting than phosphated parts and finally, a silane bath has a significantly shorter bath life than phosphates.

Due to these limitations silanes can not be effectively used to completely replace iron or zinc phosphate in most pretreatment systems. So, chemical companies continued to investigate other possible phosphate replacements. The latest development, seen throughout the pretreatment industry, is the use of fluorozirconium based chemistry to create a thin coating on parts.



## The Path to Zirconization

The use of fluoro-based acids (such as fluorozirconic or fluortitanic acid) have been used for metal treatment for decades. The most common use for fluoro-acids has been in aluminum treatment. However, making the jump from treating just aluminum, to treating parts usually treated with phosphates (which include cold or hot rolled steel, aluminum, galvanized and galvaneal steel, and other soft metals) was not easily done. Initial attempts at using fluoro-acids to replace iron phosphate resulted in unstable baths, rusty parts, and corrosion resistance less than iron phosphate.



Improvements continued to be made in fluorzirconic based formulations, resulting in the introduction of European developed nanotechnology into the American marketplace. Nanotechnology promised to exceed the corrosion resistance of iron phosphate, and in some cases could meet the corrosion resistance of zinc phosphate.

However, initial nanotechnology formulations did have limitations. First, the chemicals tended to be corrosive to mild steel washers, forcing users to modify their washers to run the product. Also, parts were very susceptible to flash rusting after treatment.

Work continued to develop an effective phosphate replacement which would not cause rusting of steel parts and the result can be seen in DuBois Chemicals' recently launched Zirconization process. Like other chemistries used as phosphate replacements, Zirconization is based on fluorozirconic acid. However, it also includes a unique blend of additives and accelerators which help promote a quicker and tighter coating on parts. This coating helps protect the parts from rusting while minimizing sludge creation.

### Setting Up and Running a Zirconization Bath

In order to properly show how Zirconization can be used as a replacement for phosphate pretreatment, it is helpful to examine how a Zirconization bath works. A Zirconization bath actually runs very similar to an iron phosphate bath and can be used in existing washers that use iron phosphate, often with no physical changes to the washer itself. Typical use concentration in Zirconization is 1-5%, which is similar to iron phosphate and some accounts have had success using concentrations as low as 0.5%.

Also similar to iron phosphate, the pH of a zirconization bath is maintained between 4.0 and 5.0. Adjustments can be made from any common alkalinity source such as potassium, sodium, or ammonium hydroxide. If the pH is run too low, a coating will not develop on the part and rust will develop. If the pH is run too high it can cause poor coating formation, and can also result in bath instability. A Zirconization bath will form a coating from any temperature from ambient to 115 °F and most users will run the system at ambient temperature. However, running at a slightly higher temperature will result in higher corrosion resistance.



**Figure 7: When the pH of a bath is at the proper pH, shown here at pH = 4.5, the solution will be clear**



**Figure 8: When the pH is above the recommended level, shown here at pH = 6.5, the solution will become turbid indicating active ingredient precipitation**

Zirconization can be used to replace a four-stage or more phosphate system and can be used in either spray or soak systems. The parts will need a cleaning stage prior to Zirconization. A clean part is essential for Zirconization to work. Also, the parts will need to be rinsed following Zirconization. Therefore, the minimum washer requirement would be a four stage system: Clean – Rinse – Zirconize – Rinse. A typical five stage system would be Clean – Rinse – Zirconize – Rinse – Final Rinse or Seal.

One negative of Zirconization when compared to iron phosphate is that a Zirconization bath is more susceptible to contamination than a typical iron phosphate bath. To prevent contamination from the cleaning stage, a possible five stage setup would be, Clean – Rinse – Rinse – Zirconize – Rinse. It is possible to run the Zirconization bath in the fourth stage, which is typically used for rinsing in an iron phosphate system and therefore is not equipped with a burner, since zirconizing is effective when run at ambient temperatures. Because rinse stages are typically designed to allow for less contact time than the pretreatment stage (30 versus 60 seconds), the chemical concentration will likely have to be increased to compensate.

### Zirconization vs. Iron Phosphate

As previously discussed, the recommended use parameters for Zirconization are very similar to iron phosphate. In most circumstances, Zirconization can be used as a drop-in replacement for iron phosphate. But, even though they may be operated in a similar manner, how will the other properties of Zirconization compare to iron phosphate?

	<b>Iron Phosphate</b>	<b>Zirconization (DuraTEC 100 Pretreat Stage)</b>
<b>Minimum Contact Time</b>	30 Seconds	30 Seconds
<b>Temperature</b>	90 - 150	Ambient - 110
<b>Concentration</b>	1 - 5%	1 - 5%
<b>pH</b>	3.5 - 6.0	4.0 - 5.0
<b>Application</b>	Wand, Spray, Soak	Spray, Immersion
<b>Minimum Process Stages</b>	1 Wand, 3 Spray/ Soak	4
<b>Sludge</b>	Significant	Minimal

**Figure 9: Comparison of Iron Phosphate and Zirconization Pretreatment Process Parameters**



One difference between iron phosphate and Zirconization is the resulting color of the parts after treatment. Iron phosphate coatings will, for the most part, be gold, blue, or purple. Zirconized parts will be gray with a light coating, or a light blue or gold with a heavier coating. In most cases, this color will not be a factor. However, it is possible that, when using a light, thin paint, that the color of the part may show through differently than before.



**Figure 10: Zirconized Steel Q-Panels**

**Operating Parameters - 3% DuraTEC 100, 80° F, and 30–90 Seconds.**



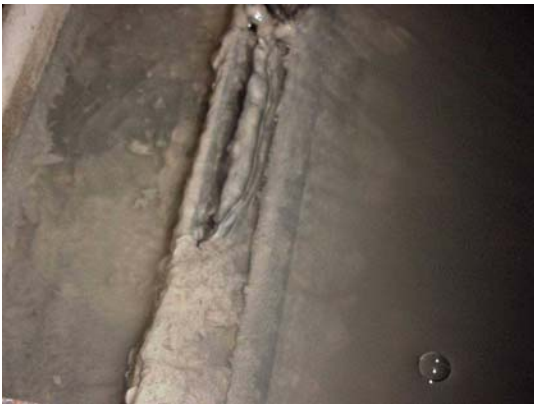
**Figure 11: Steel ACT Bonderite 1000 Test Panel (Left)**

**Zirconized Steel Test Panel (Right)**

While the Zirconization process is specially formulated to minimize flash rust, zirconized parts are slightly more susceptible to flash rusting than iron phosphate. Due to the higher presence of fluorides (a strong acid), a high iron content in an old bath, and a thinner coating, flash rust can be caused by frequent line stops and slow line speeds. Despite this, it is possible to run a Zirconization process with no rusting at all if the bath is operated properly. Running a bath at the appropriate concentrations and pH, maximizing post-cleaner rinse water quality through simple counterflow and freshwater make-up techniques, running at low temperature in both the Zirconization and the cleaning stages, and minimizing line stoppages will all help to eliminate rust.

The most obvious strength of Zirconization over iron phosphate is that the Zirconization process is phosphate-free, eliminating environmental issues associated with phosphates and producing a 'green' product. As environmental issues such as global warming gain more and more prevalence in television and print news, the demand for green products from consumers will likewise grow. In addition to being phosphate free, Zirconization is also a 'green' process due to its lower operating temperatures, helping to reduce the energy consumption and the carbon footprint of the plant where it is used. Zirconization can further be classified as being 'green' due to the fact that the chemical consumption will be less than iron phosphate.

Zirconization will also greatly reduce the sludge generated in the bath. Sludge is a common problem in phosphate baths and results in additional maintenance costs to keep the bath running by unplugging clogged nozzles and cleaning tanks filled with sludge once a bath is dumped. Sludge can also reduce part quality, as parts will have a powdery coating that will reduce paint adhesion and corrosion resistance.

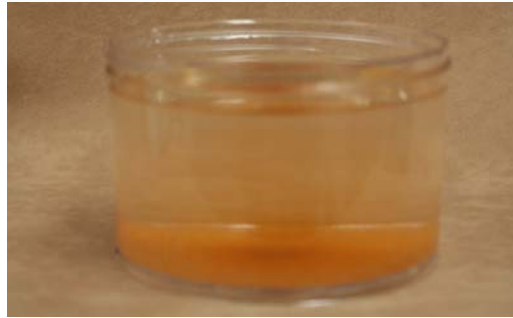


**Figure 12: Washer tank screens fouled with iron phosphate sludge, a by-product of the inefficient iron phosphate reaction**

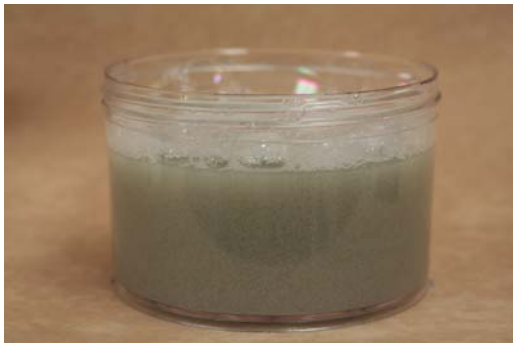


**Figure 13: Discarded spray nozzles clogged with insoluble iron phosphate sludge and hard water scale**

The results of a scientific sludge study have proven how much less sludge is generated with a Zirconization process than an iron phosphate process. This study was conducted by first preparing a 3% Zirconization bath, a 3% iron phosphate bath, and a 3% nanotechnology transition metal competitive product for comparison. All solutions were both adjusted to the midpoint in their recommended pH range. The test was run at ambient temperature. Every day for thirty days, a 4"x 6" cold rolled steel panel was placed into each solution. After 24 hours, the panel was removed and a new one placed into each solution. After thirty days, the test was ended. The following photographs show the resultant solutions.



**Figure 14: Zirconization treatment solution**  
**DuBois Patent Pending DuraTEC 100**



**Figure 15: Iron phosphate solution**

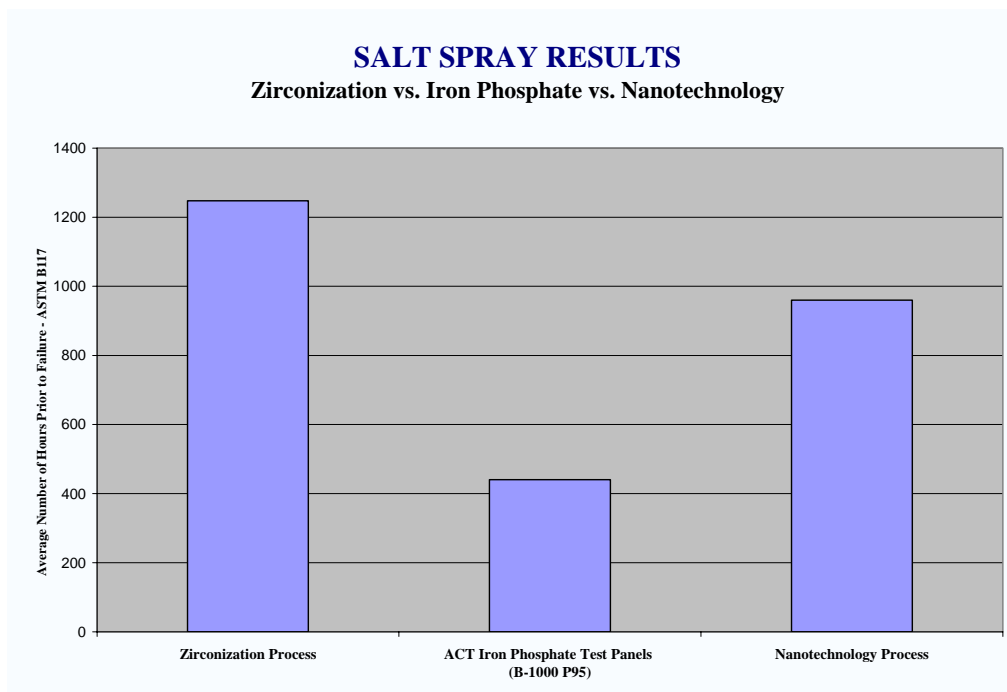


**Figure 16: Nanotechnology treatment solution**

While nanotechnology certainly produces drastically less sludge than even the lowest sludging iron phosphate chemistry, it sludges significantly more than the improved chemistry now commercially available – DuBois Dura-TEC 100. The minimal sludge produced as a by-product of the Zirconization process will result in lower maintenance costs, less downtime, longer bath life, and more consistent quality.

Perhaps the most important reason to consider Zirconization is that, at a minimum, it will meet the same quality standards as iron phosphate. In many cases, Zirconization will result in an increase in paint adhesion and corrosion resistance. At a major custom coater, a Zirconization bath was maintained at 1-2%, a pH of 4-4.5, and at ambient temperature. The washer process was as follows:

- Stage 1. Non-phosphate Low Temperature Cleaner – DuBois Met-ALL TERJ
- Stage 2. Freshwater Rinse
- Stage 3. Freshwater Rinse
- Stage 4. Patent Pending Transition Metal Chemistry - DuBois DuraTEC 100
- Stage 5. DI water rinse.



**Figure 17: Comparison of salt spray results from production**

After running through the washer, the panels had a light blue appearance and were rust-free. Two different powder coatings were used on the Zirconized parts, and the same powder coatings were applied to Bonderite B-1000 (with DI rinse) panels for comparison. The panels were tested in salt spray (ASTM B117) and were considered to have failed when their rating was below 7. The zirconized panels averaged 1248 hours prior to failure. The B1000 panels averaged 440 hours. Prior to using Zirconization, the facility had used a nanotechnology process, which averaged 960 hours of salt spray prior to failure. The zirconized panels were also subjected to cross-hatch adhesion testing and received 5B adhesion ratings.

## **Zirconization vs. Zinc Phosphate**

The benefits of using Zirconization as a replacement to zinc phosphate are even greater than they are with iron phosphate. First, there is the extra ‘green’ benefit of removing zinc from the waste stream. Second, Zirconization does not require a conditioning step, allowing for further chemical reduction and a reduction in water usage. Since zinc phosphate generally sludges more than iron phosphate, the reduced sludge generated from Zirconization will be even more pronounced.

Zinc phosphate is as susceptible to contamination as a Zirconization solution. So, a washer which runs zinc phosphate should have no problem making the switch to Zirconization. Additionally, with fewer titrations and chemicals required, a Zirconization bath will be easier to run than zinc.

The key to deciding whether or not Zirconization can be used in place of zinc phosphate depends on the quality requirements. Zinc phosphate coatings are generally used when high salt spray results are required. In some cases, Zirconization can meet these same results. In other cases, Zirconization may fall short. Testing should be performed prior to switching to Zirconization to determine if your quality standards can be maintained when switching chemistry.

## **Zirconization: The Path Ahead**

American manufacturing faces threats that are unrivaled in our history. The globalization of the economy has resulted in many manufacturing companies moving to foreign countries, where the cost of doing business is significantly cheaper. To keep plants open and or economically viable, U.S. manufacturers must cut costs while maintaining or improving quality. At the same time, they are being forced to “Go Green” due to increasing environmental concerns.

Zirconization promises to help American manufacturers face these challenges and keep their business where it belongs, on American soil. Zirconization creates a green manufacturing process that is free of phosphates and minimizes water, chemical, and energy usage while maintaining, or improving quality standards.

Certainly, some people will contend there are some advantages to traditional phosphate chemistry. First, it is readily available and is likely what a company is using now, and there is a comfort zone in dealing with a proven process. Second, the number of people available in the marketplace that have worked with traditional phosphate chemistry is large compared to those that have any experience in the newer transitional metal chemistry. Finally, change is difficult because people inherently do not like it and there may be circumstances where it is difficult because of approvals or specifications. As an example, contracts may call for resubmission of parts if a new process is adopted that could affect the quality of the parts. If the change is to something that is too new, the customer may also have misgivings, which makes it complicated for the supplier to make a change.



However, the benefits will likely outweigh the costs of change. As Hank Jennerett, a pioneer in the use of transition metal based chemistry, stated, “It is a much less expensive approach to the preparation of our parts for finishing at an increased throughput with benefits in reduced energy and water consumption and the closure of source of liquid discharge and solid waste from the plant thereby simplifying our environmental reporting and reducing compliance costs.” In one 5 month study on a production line operating 5 and ½ days a week at 20 hours a day, one user realized an annualized reduction in total process costs from \$55,000 to \$21,000.

### Total Process Costs

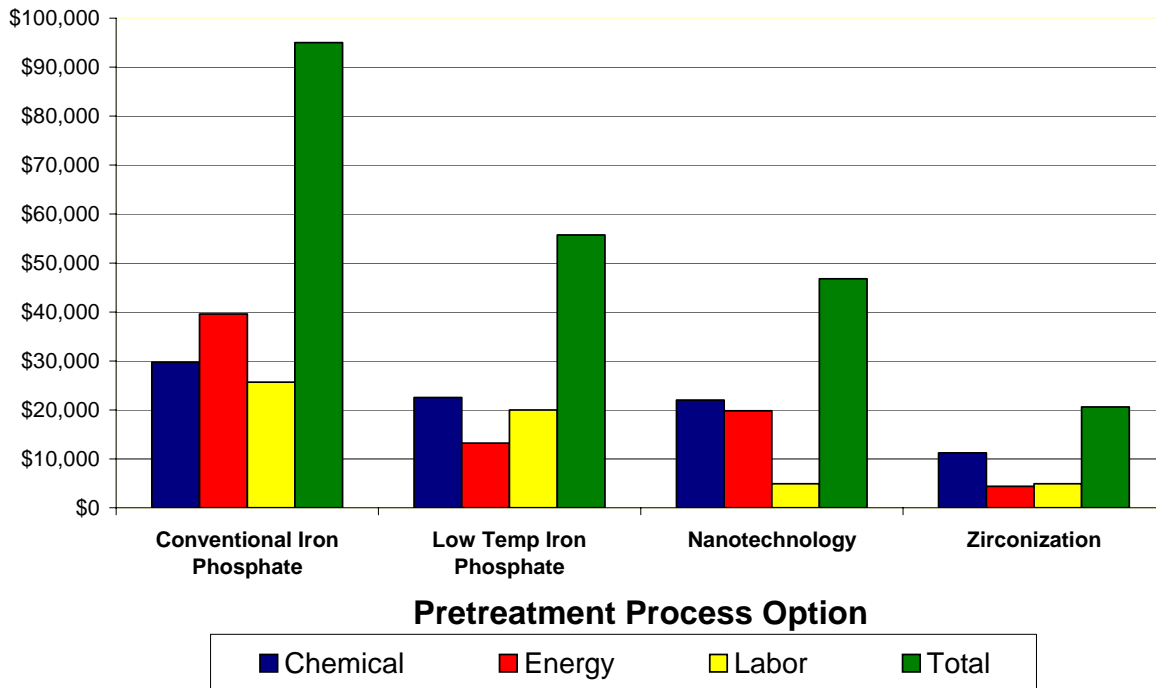


Figure 18: Total Process Cost Analysis based on historical information

Note: Pretreatment bath volume = 600 gallons, Natural Gas Cost = \$8.00/ mmBtu,  
 Labor Rate = \$35/ hour (includes hourly rate, benefits, and overhead burden)

As Ted Shreyer, Vice President of Operations for a Custom Coater that has experienced the benefits of utilizing the Zirconization Process stated, “Given the process efficiencies, environmental and cost trade offs, I cannot foresee any reason to ever switch back to iron phosphate.”

Be certain, the Zirconization Process will not be appropriate for all manufacturers, but it is a process that you can ill afford to not consider.