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## Conversion Coatings

*Types of phosphate pretreatments, how to apply them, advantages and disadvantages of each. Chromate coatings for post-treating zinc and cadmium plated surfaces...*

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CONVERT: To change into another form, substance or state. In the case of conversion coatings, the substrate metal participates in the coating reaction and becomes a component of the coating. Chemical conversion coatings are formed from the surface of the base metal outward. Therefore, the thickness of the coating is dependent upon the porosity of the coating as it forms. Once the surface is sealed from the chemical solution, the reaction stops.

Chemical conversion coatings are quite often used to enhance the characteristics of a deposit. For instance, chromate conversion coatings are applied over zinc and cadmium plated deposits to achieve higher corrosion resistance. Phosphate conversion coatings are used as a base for paint or powder coat deposits to enhance adhesion properties.

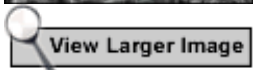
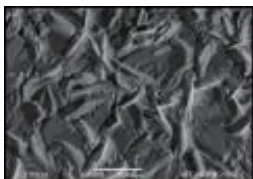
Chemical conversion coatings are an integral part of most finishing operations, serving one or more of the following functions: increase corrosion resistance, absorb lubricants, enhance appearance; promote adhesion and provide wear resistance or facilitate cold forming.

### Phosphate Coatings

Phosphating is a chemical conversion coating that transforms the surface of the basis metal into a non-metallic crystalline coating. The reaction occurs in an acidic solution containing phosphate ions. Due to the loss of hydrogen at the metal/solution interface, there is a localized rise in pH and subsequent precipitation of the coating.

Phosphate coatings can be categorized into three main types: zinc, manganese and iron. There are many proprietary formulations available for each, depending on the functional requirements of the part.

*Heavy zinc phosphate* is usually chosen for its ability to retain rust preventive oils and waxes. The heavy coating, in the range of 1,000–3,000 mg/sq ft, acts as an absorbent substrate, holding the rust preventive on the surface of the part. This provides corrosion protection in excess of 200 hr of 5% neutral salt spray exposure, depending on the formulation and concentration of the chosen rust preventive. Figure 1 shows the crystal structure of a heavy zinc phosphate coatings at 500× magnification.



Heavy zinc phosphate coatings are applied in an immersion process. Parts are run either on racks or in tumbling barrels. The bath is charged at 3–4% by volume (30–40 total acid points) and operates at 175–185°F. The bath is controlled with simple titrations that measure concentration (total acid), aggressiveness (free acid) and iron content.

Iron buildup is usually the limiting factor in the service life of the bath. When iron levels become higher than zinc, usually due to high metal throughput, coating quality and uniformity are

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Chromate conversion coating is without doubt, the most widely used “plating” for corrosion protection of aluminum and aluminum alloys. Chem Film or chemical conversion coating as the military likes to call it, is also widely known by the brand names Alodine and Iridite. All government and most commercial engineering drawings specify Chem Film using the military standard MIL-C-5541, Class 1A or Class 3.

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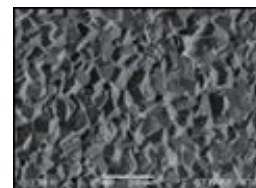
Figure 1. SEM of heavy zinc phosphate crystal (500x)

compromised. At this time, a portion of the bath can be decanted, or the bath is charged fresh.

*Calcium-modified zinc phosphate* is typically used as a base for paint or other organic coatings. The calcium co-deposits with the zinc and acts as a built-in grain refiner to form a smooth microcrystalline structure (Figure 2). Coating weights are typically in the range of 150–500 mg/sq ft, which allows for enhanced adhesion properties without being as absorptive as a heavy zinc phosphate coating. In addition, the chemical-resistant nature of calcium-modified zinc phosphate coatings confines corrosion to a limited area, often referred to as creepage, if the applied topcoat is damaged.

Calcium-modified zinc phosphate can be applied by spray or immersion. The bath is often a two-component system, with the calcium-rich component added upon start up and infrequently thereafter. Operating temperature is 150°F for spray and 170–180°F for immersion.

Iron content in the bath may interfere with grain refinement and nonuniform coatings may result. Small but frequent additions of a strong oxidizer will precipitate the iron from the solution, resulting in extended bath life.



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Figure 2. SEM of manganese phosphate crystal (500x)

*Cold-forming zinc phosphates* are used to facilitate drawing, cold heading, stamping or extruding of the basis metal. These phosphate coatings are designed to retain lubricants under severe conditions of heat and pressure during deformation. The use of the phosphate coating allows increased tool life, faster drawing speeds and more severe reductions of the basis metal. Coating weights for cold forming zinc phosphates can range from 500–2,000 mg/sq ft. The phosphating solution in this application is operated iron-free to ensure a less abrasive zinc phosphate crystal, which will not scratch dies, score or gall. A strong oxidant, commonly nitrite or chlorate, is needed to drop the iron out of the bath in the form of sludge. These operations are always immersion processes, with the optimum operating temperatures of 175–185°F.



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Figure 3. SEM of calcium-modified zinc phosphate crystal (500x)

*Manganese phosphate* (Figure 3) is most commonly chosen for its wear-resistant properties. The manganese phosphate coating not only prevents metal-to-metal contact between moving parts, such as cylinder liners, camshafts, piston rings and transmission gears, it also has excellent oil retentive properties for both lubricity and corrosion resistance. A grain refining predip is often used prior to manganese phosphating to ensure a controlled microfinish. The manganese phosphate bath is charged at 10% by volume (12 total acid) and operated at 195-205°F. The balance of the bath concentration (total acid) when compared to the bath activity (free acid) is critical to control crystal size and coating uniformity. A ratio of 5.5–6.5:1 is recommended and maintained with additions of manganese carbonate. High iron content in the bath can be lowered by treatment with hydrogen peroxide.

*Iron phosphate* is used as a base for paint or powder coat to enhance adhesion. Unlike both zinc and manganese phosphates, in which the metal cation is found in the phosphating solution, the cation of the iron phosphate coating is contributed by the basis metal. The phosphating solution typically contains alkali metal phosphate and accelerators. Coating weights for iron phosphates range from 25-100 mg/sq ft.

Application is usually in a three- or five-stage spray washer, but there are some immersion processes. For three-stage washers, the iron phosphate has an incorporated detergent system to clean and phosphate in one step. In five-stage washers, the cleaning is done separately in stage one, while the phosphate is applied in stage three. A seal is applied (either chrome or non-chrome) in the final stage to minimize under-film corrosion.

Iron phosphates are easy to control with a simple titration to determine concentration, 1–3% by volume, and pH adjustment, 4.5–5.5 optimum. Operating temperatures are relatively low, 100–130°F.

**Chromates**

Chromate conversion coatings based on hexavalent chromium solutions have been used since the 1940s to provide corrosion protection for electrodeposited zinc, cadmium, zinc die castings

**TABLE I—Chromate Conversion Coatings**

Over Zinc and Cadmium Plate				
Appearance	Activators	Function	Hours of Salt Spray (to white corrosion)	Comments

and aluminum. Hexavalent chromium films provide corrosion protection by forming an impervious layer that acts as a barrier, short-circuiting the flow of electrons from cathodic to anodic sites therefore providing electrochemical protection.

Activators, modifiers, accelerators and buffering ingredients are also incorporated into the formulas to enhance protection, appearance and adhesion properties. Table I shows the characteristics of several types of chromate conversion coatings.

Due to the toxic and carcinogenic nature of hexavalent chromates, regulations have focused on excluding its presence both in finishing shops and on the final product. "End of Life" limits for total chrome have become standards for automakers in the United States, Japan and Europe.

Active research and development has produced replacements, which are equal to or better than hexavalent chromium in corrosion resistance.

Products for electroplated zinc are generally based on the much less toxic trivalent form of chromium. The products currently on the market can meet salt spray specifications and even outperform the old technology when used in conjunction with appropriate seals.

Products for aluminum based on zirconium or titanium chemistry can likewise equal or exceed the old chromate formulations.

The operating parameters for this newer class of conversion coatings are similar, although higher concentrations and operating temperatures may be required.

Conversion coatings are economical, easy to use and offer a variety of valuable properties to extend the service life and improve the performance characteristics of the parts being treated.

Clear bright	Sulfate; buffer	Appearance and protection	12–96	Coating is leached in alkali after application
Blue bright	Fluoride; nitric	Appearance and protection	24–120	For zinc plate only; coating can be dyed for ID
Gold	Sulfate; chloride	Appearance and protection	48–96	For zinc die castings also
Olive drab	Like gold with organic acid	Protection and function	96–120	Used in military applications
Black	Like gold with silver	Appearance and protection	48–96	No chlorides in formula
<b>Over Aluminum</b>				
Clear	Phosphate and fluoride	Paint base (extrusion)		Needs hexavalent chrome seal
Clear to yellow	Fluoride; nitrates; accelerator (ferricyanide)	Paint base (general); protection		No seal needed; coating contains hexavalent chrome

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