

METAL SURFACE CONVERSION TREATMENTS

1. Phosphating

Reactive metal surfaces can be chemically treated and covered with inert, amorphous, or crystalline coatings which grow on the base metal. Phosphates represent the most important area of the conversion coatings. These coatings (qv) are applied as preparation for painting, temporary corrosion protection, lubricant carrier in cold forming, friction improver for stamping and drawing, and as insulation on electrical steels (1–3) (see also Metallic coatings; Metal treatments).

Phosphating processes began with the work of Thomas Watts Coslett. The original patent covered the use of phosphoric acid to which iron filings had been added (4). It took from 2 to 2.5 hours exposure in boiling solution to form a coating on iron and steel articles. Early improvements consisted of controlling the quantity of free phosphoric acid, thus inhibiting attack on the metal, and of accelerating the reaction by using an electric current. Concentrates from which phosphate baths could be prepared by dilution were in use by 1909. The use of zinc in the phosphate bath was patented in 1909 and the use of manganese in 1911 (5). The use of manganese dihydrogen phosphate gave rise to the process which became known as Parkerizing. Reduction in processing time from one hour to 10 minutes came through the addition of copper to the bath. This was the basis for the Bonderizing process. Addition of an oxidizing agent such as nitrate increased the reaction rate by preventing the adsorption of hydrogen on the metal surface. Paint-base phosphate coatings could be applied in two to five minutes. In 1934, this time constraint was shortened even further when phosphate solutions were sprayed onto the metal surface. Processing times as short as 60 seconds became possible.

A crucial development for zinc phosphate coatings came in 1943 when it was found that more uniform and finer crystals would develop if the surface was first treated with a titanium-containing solution of disodium phosphate (6). This method of crystal modification is a prime reason for the excellent paint (qv) adhesion seen on painted metal articles.

Modern phosphating practice involves the treatment of reactive metals with acidic phosphate-containing solutions. This produces a coating which consists mainly of phosphate compounds. Chemically, phosphating processes can be separated into two types. In processes of the first type, the metal ions of the phosphate layer derive almost totally from the substrate. These layers, known as noncoating or iron phosphates, are based on sodium and ammonium dihydrogen phosphate. Processes of the second type, on the other hand, provide metal ions for coating either partially or totally in the phosphate bath. These are the zinc phosphate processes which may contain zinc alone or modifying ions such as nickel, manganese, calcium, as well as several others.

1.0.1. The Iron Phosphating Process

Dissolution and oxidation of iron(II) to iron(III) and coating development result in the formation of an amorphous coating which contains iron phosphate, FePO_4 , as the principal coating constituent (7). In addition, some iron oxide, Fe_2O_3 , which forms from the rearrangement of ferric hydroxide, and some tertiary iron phosphate

2 METAL SURFACE CONVERSION TREATMENTS

called vivianite, $\text{Fe}_3(\text{PO}_4)_2$, are present. The oxidative condition needed for coating formation is provided by accelerators such as chlorate, nitrate, permanganate, and air entrapped during spraying.

1.0.1.1. Operation and Control. The product concentrates can be supplied either as powders or liquids. Powdered iron phosphates based on dihydrogen phosphates of sodium or ammonium form a popular line of clean-and-coat materials used in three-and four-stage lines. These formulations may also include surfactants (qv), sequestrants, solvents, inhibitors, and accelerators. High temperature iron phosphates are applied at 65.6–76.7°C for 40–60 seconds. The systems operate in the pH range of 4.5–5.5. Total acidity ranges from 6–16 points, ie, 6–16 mL of 0.1 N NaOH for a 10 mL sample of the bath determined by titrating to an end point of pH 8.2, which is faint pink with a phenolphthalein indicator. Low temperature iron phosphate processes operate at 40.6–46.1°C, at a total acidity range of 9–18 points. The optimum pH range lies between 3.7 and 4.4, having measurable free acidity, ie, titration with 0.1 N NaOH to an end point of pH 3.8. These formulations are used at concentrations similar to the high temperature variations. However, these formulations must have increased acidity and increased acceleration to compensate for the lower operating temperature. The formation of Na_2HPO_4 as a by-product of the reaction causes the pH to rise, thus acid replenishment is necessary to keep the bath in the operating range.

The application of this type of conversion coating can be by spray or immersion and is easily tailored to the needs of the user (see Coating processes). The number of stages may vary from two, ie, clean and phosphate then rinse, to as many as five, ie, clean, rinse, phosphate, rinse, and post-treat. The performance requirements dictate the number of operation stages as well as the need for a post-treatment.

1.0.1.2. Coating Characterization. As indicated, the coatings are amorphous and can therefore be characterized only by coating weight. Coating weights normally range from 0.1 to 0.8 g/m², but special formulations may yield coating weights of 1.2 g/m². For coating weight determination, coatings may be stripped from steel surfaces with a solution of chromic acid, whereas aluminum or zinc surfaces are stripped with a solution of ammonium dichromate.

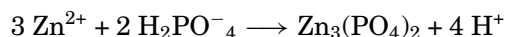
1.0.1.3. Product Utilization. Iron phosphating has been the process of choice for applications where cost considerations override maximum performance needs. Advantages are low chemical cost, low equipment cost, good paint bonding, easy control, and minimal sludge. The disadvantages, thin coatings and poorer corrosion resistance than for zinc phosphating, limit the application of iron phosphating to particular industries. Nevertheless, iron phosphates are the most widely applied conversion coatings when surface preparation for paint application is needed. Most recently developments have been aimed at formulating baths which allow coating deposition on a mixture of metals using the same coating bath. The addition of stronger etchants and the use of different accelerator systems brings these systems closer to zinc phosphates in versatility and performance.

1.0.2. The Zinc Phosphating Process

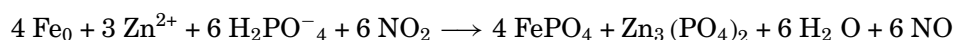
The zinc phosphating reaction involves acid attack on the substrate metal at microanodes and deposition of phosphate crystals at microcathodes (8). Liberation of hydrogen and the formation of phosphate sludge also occur. The equation for the dissolution of iron together with precipitation of dissolved iron as sludge in a nitrite accelerated system is as follows:



The NO_2 is generated when nitrite oxidizes the hydrogen produced by the acid attack on the metal surface to form water. The total reaction uses up hydrogen ions and reduces acidity. The only source of these ions at the interface is the zinc dihydrogen phosphate in solution. The result is that zinc phosphate crystallizes at the surface–solution interface to form a tightly adhering crystal layer according to the following equation:



Combining these equations gives a totalcoating reaction of



Hydrogen is prevented from forming a passivating layer on the surface by an oxidant additive which also oxidizes ferrous iron to ferric iron. Ferric phosphate then precipitates as sludge away from the metal surface. Depending on bath parameters, tertiary iron phosphate may also deposit and ferrous iron can be incorporated into the crystal lattice. When other metals are included in the bath, these are also incorporated at distinct levels to generate species that can be written as $\text{Zn}_2\text{Me}(\text{PO}_4)_2$, where Me can represent Ni, Mn, Ca, Mg, or Fe.

1.0.2.1. Operation and Control. The zinc phosphating process sequence consists of cleaning, rinsing, surface conditioning, phosphating, and final rinsing. Alkaline cleaning is used to remove soils and oils that have accumulated during storage and forming of the parts (9) (see Metal surface treatments, cleaning). Rinses between the active stages remove residual chemicals. For zinc phosphates, an effective conditioning rinse before phosphating provides the development of small, tight crystals necessary for improved paint adhesion. Conditioners, dispersions of colloidal titanium phosphate, are formulated to function consistently with equal results in hard and soft water. Finally, improved corrosion performance is most often obtained using a post-treatment or final rinse step. Some of these rinses contain chromium in mixtures of both the +3 and +6 oxidation states. Others contain chromium in the +3 oxidation state alone. Chromium-free post-treatments which match the performance of the chromium-containing post-treatments have been developed. These derive effectiveness from organic polymers which can chelate to the metal surface and to the coating (10).

The bath components for a nitrite–nitrate accelerated bath basic to this conversion coating process are (1) zinc metal or zinc oxide dissolved in acid; (2) phosphate ions added as phosphoric acid; (3) addition of an oxidant such as sodium nitrite; and (4) addition of nitric acid. Other oxidants such as peroxide, chlorate, chlorate in combination with nitrate, or an organic nitro compound may also be used.

Conventional practice is to dilute the liquid, which consists of 40–50% solids, zinc phosphate concentrate, having a density ~ 1.3 times that of water, to a 2–6% concentration with water. Soda ash or caustic soda is added to obtain the correct free acid value and the bath is then heated to the operating temperature. This is followed by addition of NaNO_2 to achieve about a 0.02% concentration. The level of free acid is critical. The free acid must be lowered to the point where zinc phosphate starts to precipitate. This is called the point of incipient precipitation (11). If the bath is neutralized too far, valuable zinc dihydrogen phosphate is lost as sludge. As the reaction proceeds and the crystalline coating is formed on the surface, the zinc dihydrogen phosphate in the bath must be replenished. Practical replenishers operate at phosphate to zinc mole ratios between 1.5 and 2.5:1 because an excess of phosphate is required to precipitate dissolved iron as the phosphate. In modified zinc phosphates, the other metals are also restored by the replenisher according to their individual incorporation in the coating.

Application of the zinc phosphate coating can be by spray or immersion. When the coating is applied by spray, the solution is quickly replaced and the coating formation takes place very rapidly. Replacement at the surface of depleted bath solution during immersion application is diffusion controlled. The rate at which the coating develops is somewhat slower. This difference in the rate of coating development is reflected in the composition of the coatings deposited. Those from the immersion application contain a large amount of iron when applied to steel and have better performance qualities than those from spray application (12). Although control parameters for the two application methods do not vary significantly, there is a difference in the replenisher formulations. This is because of a higher drag-out from the spray bath than from the immersion bath.

1.0.2.2. Coating Characterization. Phosphate coatings cannot be fully characterized by any simple methods. Characteristics such as appearance, coating weight, P-ratio (13), porosity (14, 15), coating composition (16), and crystal size combine to define a system's performance. However, measurement of any of these factors individually does not provide a sufficient indication of the coating's efficacy in meeting its intended purpose.

4 METAL SURFACE CONVERSION TREATMENTS

1.0.2.3. Modified Zinc Phosphates. Coatings on steel have been identified as hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, phosphophyllite, $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, and iron hureaulite, $\text{Fe}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$. Incorporation is also achieved when nickel, manganese, or calcium are added to the phosphating bath. Similar structures have been identified for these metals (17, 18). Modification of the hopeite structure is reflected in an increased resistance to alkalinity and a higher dehydration temperature (19). Both of these properties contribute to improved corrosion and adhesion properties of painted steel (qv), zinc, and zinc alloy surfaces (see Zinc and zinc alloys).

1.0.2.4. Product Utilization. Zinc phosphate coatings form the basis for paint adhesion in a variety of industries. These are used when long-term quality is of concern in applications such as for automotive parts and vehicles, coil-coated products, and appliances.

1.0.3. Testing of Painted Products

The enhancement of paint adhesion is one of the principal functions of conversion coating (20–22). A group of tests based on product deformation is used to test the painted product. The appliance and coil-coating industries use the mandrel bend, the cross-hatch adhesion test, and the direct and reverse impact tests. Adhesion after a water soak is judged using a cross-hatch test performed on the exposed surface.

Several accelerated corrosion tests are also employed to evaluate the effectiveness of the phosphate coating in the performance of painted products (see Corrosion and corrosion control). These tests are designed to duplicate the service environment as well as the corrosion mechanism for the painted article. In the appliance industry the tests used most often include the salt spray test, detergent immersion, water immersion, and humidity resistance. The coil coating industry uses the salt spray test, exposure in the Q-uv cabinet, ie, a test regimen involving uv light and condensing humidity at a temperature of 60°C, and humidity exposure. Testing in the automotive industry is slightly more complicated because each of the car companies has its own cyclic corrosion test. Among the cyclic tests in use are the Ford APGE Test, the GM 9511 Cyclic Corrosion Test, the GM 9540-P Cyclic Corrosion Test, and the Chrysler Chipping Test. Water immersion, humidity exposure and, to a very limited extent, the salt spray test are also being used. In addition, all industries use outdoor exposure tests for long-term evaluation of corrosion performance. However, test results from both the accelerated and in-service tests function as indicators of relative performance. These are not predictive of application lifetimes.

1.0.4. Other Phosphate Coatings

Phosphate coatings are also used as surface treatments for wire drawing, tube drawing, and cold extrusion. Zinc phosphates of heavy (10–35 g/m²) coating weights serve as the carrier for drawing compounds and lubricants. It is standard practice to use a manganese phosphate coating as an oil retaining medium on bearings or a sliding surface to eliminate scuffing, galling, and pickup, and to facilitate running in, ie, wear of mating surfaces during initial hours of operation (see Bearing materials). These coatings are usually applied by immersion at temperatures reaching 93°C at times between 5 and 30 minutes.

2. Chromating

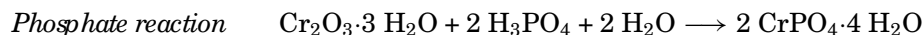
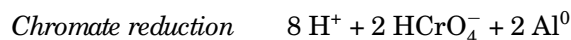
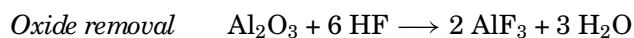
Chromating or chromating has been widely practiced in the metals industry since the late 1940s to improve corrosion resistance and performance of subsequently applied organic finishes (23). Commonly, chromates are used to treat wrought alloys, cast alloys, and coatings comprising aluminum, zinc, magnesium, or cadmium. The aerospace, transportation, architecture, appliance, marine, and electronics industries, among others, utilize chromate coatings extensively (see also Coatings, marine; Electronics, coatings).

Chromate conversion coatings are thin, noncrystalline, adherent surface layers of low solubility phosphorus and/or chromium compounds produced by the reaction of suitable reagents with the metal surface (2, 3).

The two classes of chromate coatings are chromium phosphates (green chromates) and chromium chromates (gold chromates).

2.0.5. Chromium Phosphate

Chromium phosphate treatment baths are strongly acidic and comprise sources of hexavalent chromium, phosphate, and fluoride ions. Conversion coating on aluminum precedes by the following reactions (24):



Chromium phosphate coatings can be deposited with very low (0.05–0.15 g/m²) weights to give colorless coatings for applications such as a paint base or very heavy (2.0–5.0 g/m²) weights for decorative applications.

2.0.5.1. Operation and Control. Control of a chromium phosphate conversion coating bath requires monitoring chromium and aluminum concentrations, active fluoride level, and temperature. Coating weight is very sensitive to active, ie, uncomplexed, fluoride. An innovative electrochemical method using a silicon electrode (25) is employed for measuring active fluoride. A special precaution in chromium phosphate bath operation is the formation of whitish, powdery coatings resulting from accumulation of dissolved aluminum. Commercially available proprietary chromium phosphating products typically incorporate sodium fluoride and potassium fluoride. These fluoride additions precipitate aluminum from solution as elpasolite, NaK₂AlF₆.

Typical processing steps in chromium phosphate application by either spray or immersion contact are alkaline cleaning (etching or nonetching), water rinse, chromium phosphate treatment, water rinse, and finally a deionized water rinse because acidified water is often used for paint-base applications. Usually desmutting or deoxidizing is not required for chromium phosphating after alkaline cleaning because of the strongly acidic nature of the treatment bath.

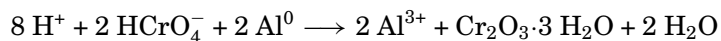
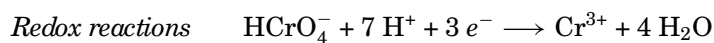
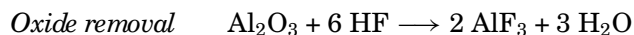
2.0.5.2. Product Utilization. The principal application for chromium phosphate coatings is as a paint base for painted aluminum extrusions and aluminum beverage can stock. In these applications, extremely demanding performance criteria are met by the chromium phosphate conversion coatings. As an example, the Architectural Aluminum Manufacturer's Association Voluntary Specification 605.2-92 requires humidity and salt spray testing for 3000 hours and allows only minimal incidence of paint failure after testing (26).

2.0.6. Chromium Chromate

Chromium chromate treatment baths are acidic and made up from sources of hexavalent chromium and complex fluoride, fluorosilicate, fluoro-zirconate, fluorotitanate, and silicofluorides. Optional additional components

6 METAL SURFACE CONVERSION TREATMENTS

added to accelerate coating rate are free fluoride, ferricyanide, and other metal salts such as barium nitrate. Conversion coating on aluminum precedes by the following reactions (2, 3, 17):



The coating composition is a combination of hydrated chromium and aluminum oxides and hydroxides, eg, $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $x = 1, 2$.

Chromium chromate coatings that have very low (0.05 g/m^2) coating weights may be deposited. These give colorless coatings. Moderately heavy (0.8 g/m^2) gold-colored coatings for maximum corrosion protection may also be deposited. Because of the hydrated nature of chromium chromate coatings, the corrosion protective properties are sensitive to elevated temperatures and prolonged heating.

2.0.6.1. Operation and Control. Control of chromium chromate conversion coating baths is accomplished by controlling chromium concentration and pH. The quality of the conversion coating is sensitive to aluminum accumulations in the coating bath as well as to rinse water purity. Sulfate contamination is a particular problem.

Typical processing steps in chromium chromate application by spray or immersion contact are alkaline cleaning (etching or nonetching), water rinse, acid deoxidize/desmut, water rinse, chromium chromate conversion coat, and a final water rinse. The performance of chromium chromate conversion coatings is strongly affected by the presence of oxides and alkali-insoluble alloying elements (smut) on workpiece surfaces. For most applications, an acidic deoxidizing–desmutting operation is required before the conversion coating stage.

2.0.6.2. Product Utilization. Applications for chromium chromate coating are extensive. Aircraft components, aluminum castings, zinc castings, magnesium castings, galvanized steel passivation, and aluminum sheet passivation are example applications for chromium chromates. In aerospace applications, the performance criteria for chromium chromate conversion coatings are extremely demanding. The Mil-C-5541E Specification includes performance criteria for salt spray resistance of 168 hours for unpainted conversion coated aluminum alloys without significant signs of corrosion. At the same time, the conversion coating must comply with a low electrical resistivity criteria to perform well in resistance spot-welding operations and electrical and electronic uses (27).

3. Anodizing

Whereas many metals can be anodized, aluminum is by far the most widely anodized metal. The anodizing process is comprised of several pre- and post-treatment steps. The anodizing step consists of placing the part to be anodized in a tank where a controlled direct current charge can be applied for a predetermined length of time. At the anode, ie, the part, the aluminum is oxidized to aluminum oxide. The hydrogen ion migrates

to the cathode, where it is reduced, forming gas bubbles that are given off to the atmosphere. As this process continues, a uniform porous oxide film is formed on the part (28). The resulting material having the anodic film can be used for structural purposes, such as aircraft parts, or for decorative purposes, such as windows or picture frames.

3.0.7. Operation and Control

The amount of current applied to the part determines the speed of which the anodic film is formed. Generally, a current density of 12.9–25.8 mA/cm² (12–24 A/ft²) is applied to produce a coating thickness of 10–20 μm (0.4–0.8 mils) per 20 minutes. Most coatings range in thickness from 5–50 μm (0.2–2.0 mils).

The temperature of the anodizing solution also has an effect on the anodic film structure. Thus chillers are used to maintain a consistent temperature in the bath while the part is being anodized, and air agitation is continuously applied to ensure a uniform temperature. The result is a consistent anodic film density of uniform pore size.

Several different acids can be used for anodizing. Phosphoric acid is employed primarily to produce a very porous film. During the anodizing step, the phosphoric acid attacks the growing anodic film, etching a portion of it away. The resulting film can be used as a paint base or adhesive bonding preparation having excellent adhesion properties. Chromic acid is used when high corrosion and abrasion resistance is needed. Most aircraft parts receive this type of anodic coating because any residual acid does not corrode the metal. The anodic film has a distinctive dull green color when chromic acid is employed. Oxalic acid is rarely used but produces a very hard, wear-resistant coating. The anodic film has a grayish yellow color. Some movable aluminum engine parts receive this type of anodizing. Sulfophthalic acid, otherwise known as duranodic or integral coloring, is used to produce a decorative anodic film ranging in color from bronze to black. This process was used extensively from 1950 to 1970 for the color of window and building fascia parts. This process consumes large amounts of electricity, however, and has become too expensive to use. Sulfuric acid is the most widely used acid for anodizing. It produces a hard, clear anodic film which can be subsequently colored using inorganic or organic coloring solutions. Sulfuric acid anodizing is used for both wear-resistant coatings and decorative purposes.

Typical processing steps in anodizing are precleaning, alkaline etching, desmutting, anodizing, two-step coloring or dyeing, and sealing. Water rinses are generally interspersed between stages. The precleaning step is critical in anodizing because it removes the shop soils and cutting lubricants before etching. Precleaning solutions are nonetching and nonsilicated cleaners, and usually contain borates to inhibit the etch. If the part to be anodized is not completely cleaned, the subsequent etching step leaves undesirable patterns on the aluminum.

In the alkaline etch step, the aluminum is given the desired appearance by either etching the surface or chemically polishing it. The alkaline etch gives the aluminum a matte finish which has a satin appearance. The desmutting step is used to remove any of the alloying elements left on the surface after the etching process. Many alloying elements, such as copper, iron, magnesium, and silicon, are not soluble in alkaline solutions. Thus these are left behind on the aluminum surface as a smut.

In the anodizing stage electrolytic reactions produce a uniform aluminum oxide layer across the aluminum surface. This anodic film is transparent and porous. The underlying matte or bright surface can be seen. After anodizing, the aluminum part can be colored or sealed.

The two-step coloring method, sometimes called electrolytic coloring, is the most popular coloring method for architectural purposes. The process involves placing the unsealed anodized parts in a bath constructed similarly to the anodizing tank. The two-step bath chemistry contains a metal salt dissolved in an acid. When alternating current is applied to the part, the metal ions are attracted to the anodic film and precipitate in the anodic pore. As the precipitation continues, the anodized part gradually increases in color until a black color is achieved showing complete saturation of the anodic pores. This coloring process can be stopped at any time during the coloring process with varying shades of color.

8 METAL SURFACE CONVERSION TREATMENTS

The use of dyes for coloring is becoming more popular because of the almost infinite range of colors that can be produced. Moreover, dyes do not need to be electrically deposited. Anodized parts are simply placed in a heated dye solution until the pores become saturated with the pigment (see Dyes and dye intermediates; Pigments).

As a final step, anodized parts must be sealed to ensure corrosion resistance of the anodic coating. Sealing involves plugging the anodic pores completely so contaminants cannot reach the base metal. A variety of sealing methods are used by anodizers (see Sealants).

4. Environmental Issues

There are three aspects of conversion coating application which impact the environment. First, high operating temperatures for cleaners and phosphating baths make these processes energy intensive. Efforts aimed at formulating systems from cleaning to post-treatment, which can be applied at temperatures ranging from 38–49°C, have had some success for iron and zinc phosphates.

Secondly, because conversion coatings rely on including such metals as zinc, nickel, and chromium, the possibility of discharge of these metals is likely. Some manufacturing locations already fall under legislation prohibiting the use of these metals. Substitutes for Ni-containing phosphates have been developed, but zinc is still part of these systems. Zinc phosphates and zinc phosphates modified with nickel are coming under scrutiny as contributors to heavy-metal contamination of water supplies. In some locations, the use of nickel is already prohibited and iron phosphates are the alternative choice. Chromium has been eliminated from post-treatment solutions and chromium-containing coatings on aluminum and zinc are being replaced with nonchromium coatings for some applications without any sacrifice of performance.

Lastly, sludge generation is an expected by-product of the conversion coating reaction. Some types of sludge are not considered hazardous waste. In many locations these can be disposed of in open landfill sites. This is expected to change and the disposal of all sludges is expected to be problematic (29). General restrictions on the disposal of sludge generated when aluminum is treated in a conversion coating system have been in place since the early 1980s. No economically feasible way to recycle conversion-coating sludge is available, although this problem occupies research efforts of companies worldwide.

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Related Articles

Metal Surface Treatments, Case Hardening; Metal Surface Treatments, Cleaning; Metal Surface Treatments, Pickling; Metallic coatings; Metal treatments