The Pretreatment System: Chemistry & Controls

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ABSTRACT

Cleaning and phosphating are essential steps in the overall coating process of steel and coated steels. The pretreatment system has to work in conjunction with the substrate being coated and the paint system being applied, to ensure the complete system meets the lifetime expectations of the end product. If one of these processes is out of control, the performance of the whole system will be affected. This paper will discuss the critical aspects of the pretreatment system with respect to individual bath chemistries, and the control parameters of each step in the process. It will also present an overview of the manual, as well as automatic process controls, used today to ensure the quality and integrity of the phosphate coating.

INTRODUCTION

When it is broken down to the basics, phosphating a surface is quite simple: first you clean it, then you treat it. If you can clean it, you can phosphate. The simplest of commercial treatment processes is a two-stage iron phosphate cleaner/coater. Depending on the specifications and performance requirements, this simple two-stage system can increase in complexity and detail to a fifteen-stage zinc phosphate process. Regardless of the number of steps, the process, control of the process and the desired outcome remain the same: enhanced paint adhesion with superior corrosion protection.

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The three main steps of the phosphate conversion coating process, regardless of iron or zinc phosphating, are: cleaning the surface, reacting with the surface, and the final sealing (post treating) of the conversion coating. Maintaining the parameters of each step is critical to attain the desired benefits. All incoming surfaces should be free of rust and uniformly active. Adequate rinsing between the various stages to remove residual chemicals and reaction products, as well as minimizing cross-contamination of the different processes, is a must.

First, we examine the simplest of the phosphating processes, iron phosphating, and then continue on to the more complex systems:

Iron Phosphating [1]

The simplest of the iron phosphate applications is a two-stage process, which includes cleaning and coating functions in a single step. This cleaner/coater process is an active iron phosphate solution with surfactants added to remove organic contaminants (protective oils) from steel surfaces. These formulations also often include sequestrants, solvents, inhibitors and mild oxidizing agents, which serve as the accelerators. Cleaner/coater processes have been expanded to three-stage applications to improve overall effectiveness of this treatment approach.

The best overall performance of any iron phosphating process is achieved when treatment is applied separately from the cleaning stage, and has a subsequent post treatment stage, as in a five-stage system. Below we examine each system and describe some of the advantages and disadvantages of each sequence:

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Two Stage: Typical Operating Parameters

    1. Clean and Phosphate: 2 - 5 minutes, 120 - 140° F,   3.0 - 5.0 %
    2. Water Rinse: 1 - 5 minutes, 70 - 110°F

    Advantages:

1. Cleans and coats in a single stage: low capital equipment costs
2. Low operational costs
3. Low coating weights due to shorter processing time
4. Simple manual controls through titration
5. Inexpensive, single stage process controllers are suitable

Three Stage: Typical Operating Parameters

    1. Clean and Phosphate: 1 - 3 minutes, 120 - 140° F,   1.0 - 5.0 %
    2. Clean and Phosphate: 1 - 3 minutes, 120 - 140° F,   3.0 - 5.0 %
    3. Water Rinse: 30 - 60 seconds, 70 - 110°F

    or

    1. Clean and Phosphate: 1 - 3 minutes, 120 - 140° F,   3.0 - 5.0 %
    2. Water Rinse: 30 - 60 seconds, 70 - 110°F
    3. Post Treatment: 30 - 60 seconds, 70 - 110°F

    Advantages:

1. Better cleaning due to longer exposure time
2. Each Cleaner/Coater stage can be run at different concentrations for optimum
     function of overall process
3. Improved corrosion performance, due higher coating weights than from two-
     stage systems, and through the use of a post treatment.
4. Wider range of end product application possibilities
5. Manual controls through simple titrations
6. Automatic process control with inexpensive, dual-stage controllers are suitable

Five Stage	Typical Operating Parameters
1. Alkaline Cleaning:	1 - 3 minutes, 120 - 140°F
2. Water Rinse:	30 - 60 seconds, 70 - 110°F
3. Phosphate:	1 - 3 minutes, 120 - 140°F, 3.0 - 5.0 %
4. Water Rinse:	30 - 60 seconds, 70 - 110°F
5. Post-Treatment:	30 - 60 seconds, 70 - 110°F

Advantages:

1. Improved cleaning with the use of a separate, dedicated stage
2. Improved corrosion performance, due to higher coating weights than two- or three-stage systems, and the use of a post treatment
3. Widest rage of application possibilities, metal substrates and end products
4. Manual controls through simple titrations
5. Wide range of process controls selection, including those with data acquisition/SPC capabilities are available options

The disadvantages for all three systems remain the same, only varying in degree:

1. Overall quality will vary depending on the number of stages
2. Limited end product use, based on the processes' inherent performance capabilities
3. Overall performance closely tied to the initial quality of the substrate being treated

It is essential to control the concentration of the process solution to ensure the essential components are available to deposit the coating. Once the process is set up to optimal conditions and the controls maintained, the desired results can be achieved consistently. Typically, the manual controls of an iron phosphating process include: pH, total acid and free acid or acid consumed. The overall concentration of the working bath is measured by a total acid titration, while the activity of the phosphating solution is controlled by pH, typically in the range of 4.0 – 5.5. At the lower pH values, 4.0 - 4.5, the acidic attack is more aggressive, and, as the pH increases, the reaction proceeds more slowly. This activity can also be measured by performing a free acid or acid consumed titration. To maintain proper control of the iron phosphate bath, routine checking of the total acid will serve as a general indicator of the concentration of all bath components. The additional check of the iron phosphate bath pH and/or free acid or acid consumed can be used as an indicator of excessive alkaline cleaner drag-in from previous process steps. If side additions of acid are used to maintain the pH, then this corrective action can result in all the bath components, including process accelerators, to drop in concentration. Proper addressing of problems in pH control of an iron phosphating process are best approached by correcting cross-contamination issues.

The use of automatic process control equipment will, in most cases, center around conductivity measurements of the operating bath, with the control logic of the equipment attempting to correlate bath conductivity to the overall product concentration in solution. Measuring a bath's conductivity is an indication of the concentration of all soluble bath components capable of conducting an electrical current.

In the case of iron phosphating processes, measuring bath conductivity is very closely related to the overall concentration of the total acid components in the solution. This is primarily due to the fact that there are little or no by-products formed during an iron phosphate coating process that contribute to any changes in operating bath conductivity.

The introduction of contaminants into an iron phosphate bath, for example from poor rinsing prior to phosphating, will cause an imbalance in the correlation of bath conductivity to total acid component concentration. This will result in line operators having to make frequent changes to a control set point of the automatic process control equipment, in order to main a total acid consistency. This is an undesirable corrective action, and again, the source of contamination drag-in to the iron phosphating bath should be eliminated instead.

A secondary control channel for pH measurement of the iron phosphating bath can be useful in tracking contamination levels in the tank, and making the corrective side additions of acids referenced above. Even with the incorporation of pH measurement, the overall automatic process control equipment requirements of an iron phosphating process are minimal, and simple, inexpensive control systems are invaluable investments in process and quality control.

In summary, when under proper control, iron phosphates can offer good physical results, and, when coupled with a strong paint system, can provide very good corrosion performance. However, since iron phosphates are thinner coatings than zinc phosphates, weaker corrosion resistance may limit end use applications for this process.

Cleaning - the most important step in any phosphating process:

Although separate cleaning steps are employed in some iron phosphate systems, they are practically essential for a zinc process. Unlike iron systems in which most of the soluble components become insoluble and part of the coating, zinc phosphate systems incorporate soluble metal phosphates in solution that make up the coating composition along with the ions from the substrate being treated. These metal phosphates are insoluble in an alkaline environment, so that a separate cleaning stage must be employed. Therefore, the first critical step in this type of phosphate system is the cleaning stage. If the cleaner does not fulfill its function then the subsequent steps in the process will not adequately protect the metal surface.

The role of the cleaner is to be able to remove any and all soils. Typical soils that enter into the phosphate washer include rust preventative oils and lubricants, metal forming blends, forging,

polishing and buffing compounds, rolling oils used in the mills, as well as inks used to mark metal surfaces. Any and all these unwanted materials have to be removed from the surface prior to the deposition of any phosphate coating

There are three general mechanisms taking place during cleaning to remove all soil types from the metal surface:

1. Detergency
2. Chemical Reaction
3. Mechanical Action

Detergency is derived from cleaner additives that emulsify and actually lift organic soils from the surface, and then disperses these oils in the main body of the cleaner. Kinetic energy imparted on the work surface during the spraying of the cleaning solution plays a key role in the emulsification process. These additives are the surfactants used in a particular cleaner formulation designed to meet the needs of each individual paint line process, and fall into one of three classes: Cationic, anionic, or non-ionic. This particular cleaning mechanism typically does not change the surface characteristics of the substrate.[2]

Chemical reactions can be utilized in cleaning by choosing cleaner components that react with the soil, so that it is lifted and removed from the surface through this reaction. Highly caustic additives in cleaners serve this function.

Mechanical action is achieved by the impingement on the surface of either a massive volume of solution or through the use of extreme pressure. In severe cases, actual contact with brushes may be required. In any case, physical contact with the soil affects its removal. As stated earlier, mechanical action coupled with detergency forms the basis for most soil removal during a phosphate cleaning process.[3]

The cleaners used in the metal finishing industry today can be assigned to one of three general categories:

1. Neutral cleaners.
2. Acid cleaners.
3. Alkaline cleaners.

Neutral cleaners are typically used to clean lightly soiled surfaces and offer some in-plant rust protection. The rust protection properties of the neutral cleaners allow for their use as "in-process" cleaners, were surfaces are machined or worked, then transferred to other areas of the manufacturing plant awaiting final assembly. The rust preventative property of the neutral cleaner reduces the potential for any oxidation of the metal surface to take place during this waiting period.

Acid cleaners are used to remove surface oxides, such as heat, weld and laser scale on incoming parts, as well as general equipment maintenance cleaners. Acidic cleaners were initially designed as

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maintenance cleaners, used to remove any scale build up within the washer or external heat exchangers. This scale build up can be due to hard water salts or sludge deposition during normal processing operations. Lately, the acid cleaners are being utilized to a greater extent, due to the increased frequency of laser cutting in the fabrication departments of manufacturing operations. If left on the surface, the laser scale will not fully adhere to the surface, and, if subsequently coated over, paint loss will result.

The real workhorses in today's phosphating operations are alkaline cleaners. They are versatile enough to effectively clean the surface by lifting the soil up and dispersing it into the main cleaner body. Once the soil has been removed, it is held in solution until it is removed by either mechanical means, such as a thermal oil separation or through the use of ultra-filtration, or the simple expedient of overflowing the cleaner tank to remove the separated oil that float on top of the cleaning solution.[4]

In evaluating a cleaner, the cleaner must be able to clean all surfaces, of all soils, on all applicable substrates, ranging from steel and galvanized to the alloys such as zinc/iron, zinc/nickel etc. The cleaner must be:

1. Versatile
2. Durable
3. Low foaming
4. Easily rinsed

In order to clean off all surfaces, the cleaner must be versatile as well as durable. These two characteristics must work together in order for the cleaner to operate efficiently and economically. By varying the combinations and quantities of alkaline components in the cleaner, one can achieve the versatility and durability required in today's production lines.

Since cleaners are sprayed, a means to control foaming is necessary so the material will stay in the tank. Certain surfactants are designed to inhibit the generation of foam, so when used in combination with other surfactants this controlled foam characteristic can be achieved. A cleaner must also show good rinsability. Any cleaner residual left on the surface must be able to be rinsed off in order to ensure a good clean surface that will not inhibit the formation of a good phosphate coating.[4]

Manually controlling the cleaner baths, as with other chemical stages, amounts to an acid/base titration to a pH endpoint. In most cleaners, the free alkalinity is the control point while the total alkalinity is used to help determine the bath's level of contamination. As the cleaner bath ages, the pH and free alkalinity drop while the total alkalinity remains the same, as free alkalinity components of the bath are consumed in combining with soluble soils in the bath. When the bath is replenished with fresh cleaner concentrate, both free and total alkalinity increase and pH rises. If one measures the free alkalinity and total alkalinity, and then divides the total by the free, then an alkalinity ratio will result. As a guideline, it is sometimes suggested that when this ratio exceeds 3:1, the cleaner should be discarded and recharged. The guidelines for maintaining cleaner baths are this simple and

when properly followed and maintained, will ensure a clean surface for the subsequent stages.

Earlier it was stated that measuring bath conductivity is the basis for most automatic chemical control processes on a phosphating line. This remains true for cleaners, with one additional complication: both free and total alkalinity components in the cleaning bath (or free and total acid components) are soluble in the cleaning solution, and both contribute significantly to the overall bath conductivity. The complication arises as one attempts to control the active cleaning solution concentration, free alkalinity, while total alkalinity is either stable or rising from the increase in contamination loading to the bath.

The key to managing both the concentration (free alkalinity) and contamination (total alkalinity) through a single conductivity measurement lies in two areas: 1) Maintaining a consistent level of contamination in the cleaning solution, and 2) The choice of control algorithms to use in interpreting the changes of the single conductivity signal, and then taking the appropriate responses. Maintaining a consistent level of contamination requires consideration from a simplistic mass balance approach that the rate of new contaminant additions to the bath from normal cleaning needs to be equivalent to the rate of discharge from the bath these same contaminants. The latter is achieved through the utilization of what is described as a system of counter flow and auto-draining of cleaner baths and rinses, where a portion of the bath is discarded in small, continuous amounts. The automatic process control system should be designed with provisions to open and close solenoid valves that add fresh water to the bath, discard some of the bath to the waste collection system, and/or pull rinse water into the tank from the subsequent rinse stage. In designing a system for water and waste management in the process control system's control algorithms, one must consider the entire process and how optimum usage of water can best be obtained.

While more complex zinc phosphating line layouts demand that a higher level of automatic control equipment be used for complex process management, smaller lines can employ the same inexpensive control units used in iron phosphating processes. Detailed automatic control systems have been primarily PLC (Programmable Logic Controller) based in the past, although more recent advances in PC (personal computer) based control systems have appeared in the marketplace. Whichever style of system is used, it is the algorithms, or the lines of logic, used within the processor that really determines the cost-effectiveness of the control system. These algorithms basically determine control responses above and below set points, and how far the bath conductivity should be allowed to move away from the set point, and at what rate.

For the most sophisticated of automatic control options, recent developments in auto-titration techniques have been employed. Here, a continuous sampling of the bath is automatically made and titrations that are normally performed manually are done within the auto-titration system. Both free and total alkalinity titrations can be performed, as well as methods for determining the precise content of surfactants remaining in the working cleaner bath. This option for automatic control systems is quite cost prohibitive though, in terms of just how much improved control can be realized over simple conductivity measurements and the use of appropriate control algorithms.

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The phosphating process has certain prerequisites in order to achieve maximum benefits. As described earlier, the processing sequence requires cleaning, rinsing, phosphating and final rinsing. Incoming surfaces should be free of rust and uniformly active. Adequate rinsing between the various stages to remove residual chemicals and reaction products are a must. Zinc phosphates require an effective conditioning rinse prior to phosphating to provide for the development of a small, tight crystal formation necessary for improved paint adhesion. [5,6]

The Zinc Phosphating Process [7]

Zinc phosphates have become the preferred pre-paint treatment in the metal finishing industry, under a wide variety of paint systems. The reason for this is that they provide better corrosion resistance and paint adhesion when compared to iron phosphates under similar demanding conditions of exposure. Application can be either by spray or immersion. Spray systems are typically 6 to 8 stages while immersion systems can range from 10 to 15 stages. With the size and complexity of the overall system, control of zinc phosphate stage is critical.

The bath components that are basic to this conversion coating process are:

1. Various metal ions such zinc, nickel, manganese dissolved in acid,
2. Phosphate ions, added as phosphoric acid,
3. Nitric acid, and,
4. Oxidants such as sodium nitrite, sodium chlorate, chlorate in combination with nitrate, or an organic compound.

In spray or immersion systems, the initial reaction step involves an acid attack and oxidation on the metal surface. The mechanism of coating formation is very different in zinc phosphating from that of iron phosphating. The fundamental difference lies in the fact that the zinc phosphate coating is formed mainly from the metal in the bath and not from the metal surface being treated, as is the case in iron phosphating. In addition, the zinc phosphate coating is crystalline and in heterogeneous crystalline union with the metal. A simple explanation of the mechanism is that the attack on the metal surface alters the pH at the interface. The acidity is reduced and zinc phosphate crystallizes at the surface/solution interface to form a tightly adhering crystal layer. Hydrogen is prevented from forming a passivating layer on the surface by the 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 also be incorporated into the zinc phosphate crystal lattice.

The constituents in a working bath may vary widely in the many different commercial and proprietary processes used today. However, from the mechanism explained above, it is clear that 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 (PIP). If the bath is neutralized too far, valuable zinc phosphate will be lost as sludge, even though the bath may still function.

The mechanism of the zinc phosphating reaction involves an acid attack on the substrate metal at an anodic site. Deposition of phosphate crystals then occurs at the cathodic site. This reaction also involves the liberation of hydrogen and the formation of phosphate sludge.

An example of this simplified mechanism is shown in figure I:

1. The Free Acid Etchs The Substrate at the Anode.
2. An electron shifts to cathode creating H+, hydrolizing water.
3. H gas and OH- forms creating a localized area of high pH.
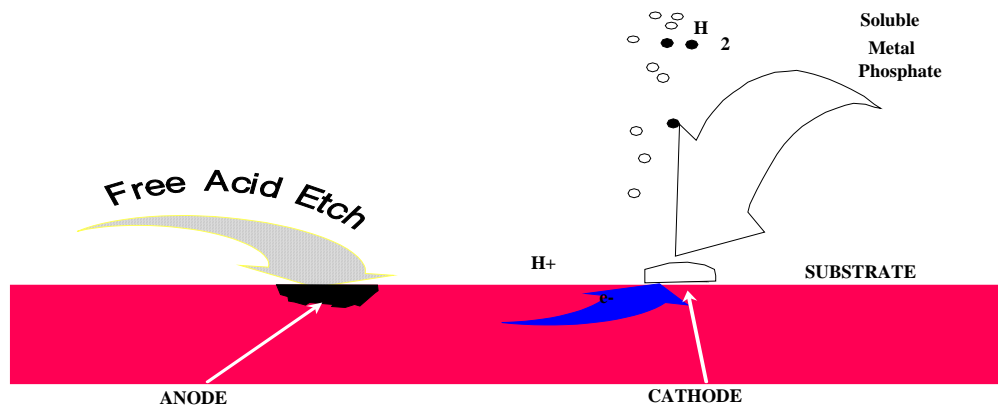**4. Coating is deposited**

Figure I
Phosphate Coating Mechanism

If all the reactions taking place simultaneously in a zinc phosphate bath were combined, a general equation for the reaction on steel would be:

$$4 \, Fe + 3 \, Zn^{+2} + 6 \, H_2PO_4^{-} + 6 \, NO_2 \longrightarrow 4 \, FePO_4 + Zn_3(PO_4)_2 + 6 \, H_2O + 6 \, NO \qquad \text{(Equation 6)}$$

When present in the operating bath, other metals ions such as nickel, manganese and calcium become part of the overall coating. These metal ions replace a single Zn^{+2} to form a $Zn_2Me(PO_4)_2$ where Me represents one of the other metals. Incorporation of these other metal ions into the coating changes the coating characteristics.

The manual controls for the zinc phosphate process must be watched more closely than in the iron phosphating process. This is due to the soluble metal phosphates in solution, which become part of the coating during the deposition process. The controls for the zinc process are free acid, total acid and accelerator level. The free and total acids are measured by either titration or pH. The free acid endpoint is at a pH of 3.8, while the total acid endpoint is 8.2. Accelerator concentrations are measured either by titration or through the use of a saccharometer. Although the controls are fairly simple, the phosphate coatings cannot be fully characterized by any simple methods. Characteristics

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such as appearance, coating weight, P-ratio [9], porosity[10,11] and crystal size combine to define a system's performance [12]. Measurements of these resulting parameters individually often do not provide a sufficient indication of the coatings' efficacy.

Automatic controls employed to manage zinc phosphating baths again are based around conductivity measurements. Additional input to larger control systems can be pH and ORP (oxidation/reduction potential), to assist in the control of free acid and accelerator levels respectively, but are typically not found in simpler systems. Auto titration units have been used to measure not only these three variables, but in high-end production lines checks on the actual level of zinc in the bath have been made. However, a typical control scheme for zinc phosphating bath maintenance can be as simple as using a single conductivity measurement to control total acid in the bath, and to use the time duration of these additions to proportionately add other bath components (accelerator, pH adjust, fluoride, etc.).

The zinc phosphating process must be maintained within the given operating specifications of the proprietary product in order to offer the optimum performance. While iron phosphating offers a little more latitude in terms of operation and controls, the zinc phosphating offers better overall performance, but under tighter controls.

Post Treatments

The last processing stage in a phosphate system is the final rinse or post-treatment stage where a chromium containing or a chromium-free "sealing rinse" is applied to the developed phosphate coating. This final treatment can enhance the corrosion resistance and humidity resistance by ten-fold compared to conversion coatings without a final rinse. Comparative testing shows that when the post-treatment rinse contains a trivalent, a hexavalent, a trivalent/hexavalent combination or certain other inorganic or organic compounds, the corrosion performance of painted surfaces is improved dramatically when compared to a deionized final water rinse[14].

Mechanisms of the function of a chromium containing rinse include:

1. Traces of metal ion, such as calcium and magnesium stemming from hard water impurities, as well as the by-products of a conversion coating process, are converted to insoluble chromates.

2. Minute areas of the surface not fully covered with zinc phosphate can be passivated, or "sealed", by these rinses.[13]

The term "sealing rinse" was used to suggest the latter mechanism. The mechanism of the rinses based on other inorganic salts parallels that for chromium containing rinses, although the suggestion has been made that there might be some ion exchange between the phosphate coating and the metal ions in the rinse to improve corrosion resistance. However, the function of the final rinse processes that contain organic compounds is significantly different. For these processes, the proprietary

polymers that are used have been chosen because of their ability to chelate metal ions. This chelation, or "binding", takes place either in the coating itself, or on areas of the metal surface which has not been fully covered by the phosphate coating. This final treatment results in a greater passivation of the metal surface and a physical barrier to diffusion of oxygen and water, both of which are reaction routes needed for corrosion to take place.

The manual controls of the final rinses again are simple and based on both pH and concentration. For those that contain an organic polymer, temperature control is also needed. Because of the deleterious effect of contamination, the working baths of these processes are generally dumped on a regular basis.

When a deionized water rinse is the only treatment after the phosphate stage, extremely tight control must be used to insure the quality. Typically several stages are employed to minimize the contaminants being dragged in from prior stages. To reiterate, the corrosion resistance is improved significantly when some type of chemical post-treatment is applied.

Summary

Within the overall phosphating process, the most important step is cleaning, since it is responsible for the removal of all types of soils on all incoming surfaces. If the surface is properly cleaned and rinsed of any and all residual chemicals, a uniform phosphate coating will result. The phosphate coating is generally post-treated with a product containing either an organic polymer or inorganic components. Production experience has over time demonstrated that a uniform phosphate coating, iron or zinc, has a significant impact on the resulting quality and performance of the end product in the field. Although manual controls through simple titrations and pH measurements are sufficient to maintain the integrity of all pretreatment processes, utilizing automatic process controls on phosphating lines can better ensure consistency and economical usage of both chemicals and water.

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