

## Zinc Phosphate Coating in Corrosion Control – A Review

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### Abstract

Due to its wide areas of applications, ready availability and affordability, mild steel has become a very versatile metal in the industry, but it is usually exposed to different environments that can corrode it, thereby affecting its properties and performance. Hence, effective metal corrosion control is required before or during mild steel application.  $Zn_3(PO_4)_2$  coating is a preferred method for surface treatment and finishing of both ferrous and non-ferrous metals, being highly regarded for its efficiency, rapid operation and ability to provide outstanding corrosion and wear resistance, adhesion and lubricative properties. In this review, components of  $Zn_3(PO_4)_2$  bath, its detailed process, adsorption mechanism on metal surfaces, applications, thermodynamic and kinetic properties, are considered.

**Keywords:** coating; corrosion; metal;  $Zn_3(PO_4)_2$ .

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### Introduction\*

One effective way of controlling corrosion is through chemical conversion coating. Coatings are insoluble, inorganic amorphous or crystalline surface films that are produced on a metal surface as a result of the chemical reaction on it. The film (non-electrolytic) forms on the metal surface in contact with a corrosive medium (electrolyte). That is, coating process involves subjecting a metal surface to chemical or electrochemical treatment, to create a protective covering which makes it less reactive in harsh environments [1]. The conversion treatment is an excellent option for retarding metal corrosion, as it is inexpensive, simple to make and highly effective [2].

Chemical conversion process is popular, since it quickly produces coatings. A crucial element in the formation of the final protective film in these coatings involves the conversion of a portion of the base metal during the process. This transformed component exhibits significantly reduced reactivity to subsequent corrosion compared to the original metal surface. By giving the metal surface an equal potential, this film balances the potential of nearby cathodic and anodic galvanic corrosion sites [3-4].

Chemical conversion coating techniques are divided into three groups, based on their main components: phosphates, chromates and oxalates. Phosphate

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\*The abbreviations and symbols definition lists are in page 375.

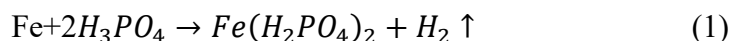
conversion coatings have been considered as viable substitutes to chromate ones, due to their reduced toxicity and satisfactory properties [1].

### Phosphate coatings

Phosphate coating is the most commonly used or popular type of steel surface treatment, due to its excellent adhesion, high corrosion resistance, enhanced abrasion resistance of the structure and affordable manufacturing costs [5]. The expression “phosphate coating” denotes the process of treating a metal surface to generate a continuous and strongly adherent insoluble compound that possesses higher absorbency compared to the underlying metal [6].

Phosphating is widely used for preparing metallic surfaces, as it provides greater corrosion resistance and is typically used for conversion coatings. Its high quality is achieved with the addition of certain constituents in the right proportions to the phosphate bath, such as oxidizing agents ( $\text{NO}_3^-$  or  $\text{NO}_2^-$ ), activators ( $\text{ZnCl}$  or  $\text{ZnF}$ ) and stabilizing agents (such as  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$ ). When phosphate treatment is of high quality, steel’s ability to resist corrosion and adhere to the paint layer increases [7].

Conventional phosphating baths consist of diluted solutions based on  $\text{H}_3\text{PO}_4$ , which incorporates one or more alkali metal or heavy metal ions. These baths predominantly contain primary phosphates of metal ions and free  $\text{H}_3\text{PO}_4$ .



Eq. (1) represents what occurs when a steel panel is added to the phosphating solution, and free  $\text{H}_3\text{PO}_4$  in the bath prompts Fe dissolution at the microanodes on the substrate. At micro cathodic sites, hydrogen evolution takes place [8].

Insoluble heavy metal tertiary phosphates are quickly transformed and deposited, due to the altered hydrolytic equilibrium brought on by the pH change between soluble primary phosphates and insoluble tertiary phosphates of heavy metal ions present in the phosphating solution [9].

The effects of applying phosphate conversion coatings at 25-95 °C have been researched in existing literature. Corrosion resistance is influenced by the coating’s thickness, microstructure, surface treatment, density and coverage. The coating’s ability to prevent corrosion decreases with growing porousness and cracking [10]. There are few shortcomings for this form of coating. Proper disposal or treatment of waste generated from the coating process is required to prevent hazardous chemicals from causing environmental pollution to plants and animals. The sludge obtained from the process is hazardous in nature [8]. Also, the metal surface has to be thoroughly cleaned and treated before the phosphate coating application, since the presence of contaminants may result in poor adhesion, which reduces its effectiveness [14].

### Types of phosphating

The three main types of phosphate coatings are  $\text{Fe}_3(\text{PO}_4)_2$ ,  $\text{Mn}_3(\text{PO}_4)_2$  and  $\text{Zn}_3(\text{PO}_4)_2$ . Each type has specific advantages, depending on the desired application and environmental conditions.  $\text{Fe}_3(\text{PO}_4)_2$  is excellent for preparing metal surfaces

before painting, thereby providing moderate corrosion resistance.  $Mn_3(PO_4)_2$  coating provides good resistance to wear, being used in firearms and other machinery that require lubrications.  $Zn_3(PO_4)_2$  coatings offer good films that promote excellent metallic painting. Therefore, they are widely applied in industries [1].

#### *Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> coatings*

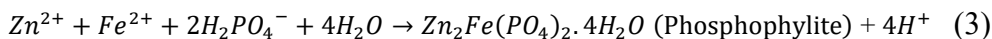
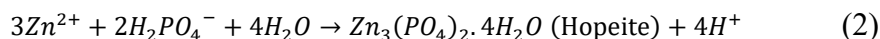
Although  $Fe_3(PO_4)_2$  coatings have lesser corrosion stability than  $Zn_3(PO_4)_2$  coats, they have also occasionally been used. In comparison to the technological process used to create  $Zn_3(PO_4)_2$  coatings,  $Fe_3(PO_4)_2$  coats are much simpler, use much less equipment and require simpler wastewater treatment [10].

#### *Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> coatings*

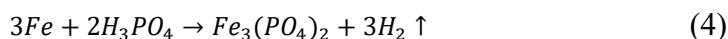
This form of phosphating provides good absorbency onto the metal surface. In terms of results, it is preferred over  $Fe_3(PO_4)_2$  coatings, but not over  $Zn_3(PO_4)_2$  ones.

#### *Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> coatings*

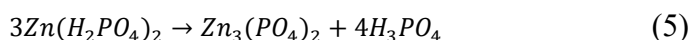
Due to their excellent corrosion and wear resistance, good lubrication, adhesion and affordable application,  $Zn_3(PO_4)_2$  coatings have been used extensively [11]. Eqs. (2-3) represent potential outcomes of  $Zn_3(PO_4)_2$  coating bath reaction:



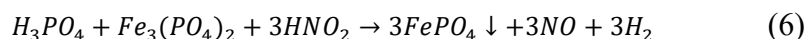
In the mechanism of  $Zn_3(PO_4)_2$  coating, the metal reacts with  $H_3PO_4$  to produce  $Fe_3(PO_4)_2$ , as in Eq. (4).  $Fe_3(PO_4)_2$



The soluble primary  $Zn_3(PO_4)_2$  transformation to an insoluble tertiary  $Zn_3(PO_4)_2$  is depicted in Eq. (5).



Formation of sludge ( $Fe_3(PO_4)_2$ ) occurs as in Eq. (6).



### **Components of $Zn_3(PO_4)_2$ coating bath**

#### *Diluted $H_3PO_4$*

$H_3PO_4$  is one of the substances used in the phosphating solution to regulate free acid and total acid values, which relate to the concentrations of free and total phosphates present in the solution, respectively [1].

#### *Accelerators*

The primary goal of adding the accelerator is to reduce the coating time during phosphating, which ranges from sec to h. Oxidizing agents such as  $CrO_3^-$ ,  $NO_3^-$ ,

$\text{NO}_2^-$  or a mixture of them affects depolarization of hydrogen evolution reaction by consuming hydrogen ions at cathodic sites. Short phosphating times are often advantageous for industrial applications. To speed up coating formation, accelerators like nitrate, nitride and chlorate should be added to  $\text{Zn}_3(\text{PO}_4)_2$  coating bath [12]. Reduction in the coating time implies less energy consumption, which eventually amounts to lower operating costs.

#### *Activators*

According to research, excellent phosphating can only be produced when the substrate's etching rate is substantially lower than the one at which coatings form in the solutions [13]. That is, the addition of activators eases the preparation of the metal surface before surface coating. Fluorides are normally included as activators in  $\text{Zn}_3(\text{PO}_4)_2$  coating solutions.

#### *Coating agents*

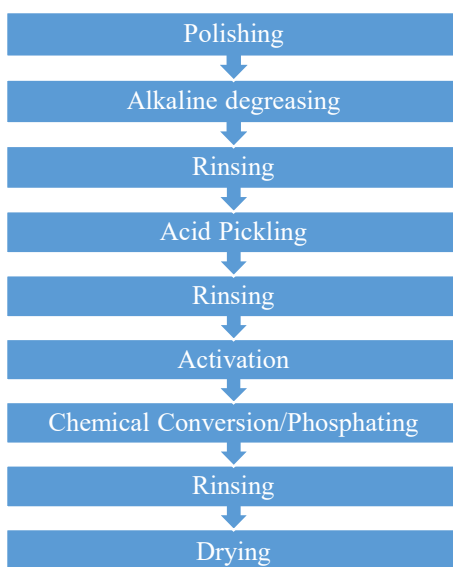
Among other components, phosphate coating consists mainly of hopeite, which is extensively used to prevent steel, Al alloys, and Mn alloys corrosion. Hopeite's non-toxic and anticorrosive qualities make it a suitable coating substitute for Cr conversion coating. Coating agents such as ZnO and  $\text{Zn}(\text{NO}_3)_2$  are normally used [1, 14].

#### *Other agents*

Organic acids can combine with some insoluble phosphates to produce a soluble complex that will stabilize phosphating bath [15]. Some additives such as Ni, Mg, Ca and Mn can be added to  $\text{Zn}_3(\text{PO}_4)_2$  bath, to increase its adhesion and corrosion resistance. The performance of the finished coating can be significantly improved through the addition of compounds such as  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mo}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  [16].

#### *Detailed $\text{Zn}_3(\text{PO}_4)_2$ coating process*

Complete phosphating process is shown in Fig. 1.



**Figure 1:** Complete phosphating process.

The flow diagram can be modified including certain pre-processing and/or post processing stages [17].

#### *Polishing*

Poor metal surface preparation is often the cause of coating failures. The metal is subjected to polishing using emery paper of various grades, to achieve the desired smoothness. This process prepares the metal surface for the phosphating process, removing any rust, dirt or impurities, thus activating it [11].

#### *Alkaline degreasing*

Prior to the formation of a chemical film on the work piece, it is required to eliminate surface grease, dust, rust, metal filings and other contaminants. Chemical alkaline degreasing ensures the smooth progression of the chemical reaction between conversion film and metal substrate, facilitating their strong bond. Degreasing can be done preferably in a NaOH solution. Also, mechanical degreasing techniques. Mechanical degreasing techniques, which include manual brushing, sand and shot blasting, can be carried out [8].

#### *Rinsing*

It is preferably done in deionized water and alcohol, to ensure that the alkaline used for degreasing does not remain on the metal surface and ends up contaminating the phosphating process.

#### *Acid pickling*

Using HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> for acid cleaning or pickling is a highly efficient way to get rid of mill scale and rust. In the presence of inhibitors, diluted solutions of H<sub>2</sub>SO<sub>4</sub> and HCl (5–10 wt%) are employed to remove inorganic pollutants by reducing them their ferrous salts [3, 8].

#### *Second rinsing*

This second rinsing is carried out to remove the acid used for pickling. The phosphating process can become contaminated by drag-in from HCl stage, which can cause issues like an uneven coating, which makes bath control difficult [4].

#### *Activation*

This procedure creates tiny active crystal centers on the metal's surface, which ultimately aid in creating a uniform and consistent phosphate coating. The two types of activation are acidic and alkaline [6].

#### *Phosphating*

All phosphating compositions are basically diluted solutions based on H<sub>3</sub>PO<sub>4</sub>, which also contains alkali metal ions and suitable accelerators [18]. Performing phosphating on both ferrous and non-ferrous metals is effective. Both spray and immersion techniques can be used to deposit phosphate, and the choice of the best technique relies on the size and form of the substrate to be coated, and in the

intended application of the coating [8]. Temperatures from 30 to 99 °C are considered adequate for phosphating process, while processing times range from a 30 sec to 6 h, depending on the phosphating bath constituents [8].

#### *Third rinsing*

After phosphating, the surface must be properly rinsed with deionized water, to eliminate any soluble salts, acid residues and non-adherent particles that may otherwise encourage blistering of the finishing paint coatings [4, 8, 19].

#### *Drying*

In locations with ideal evaporation conditions, warm air circulation fans and compressed air blow offs are the most economical techniques. Phosphate panels are prepared to apply additional treatments, such as paint and oils [8].

### ***Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> conversion coating characterization***

#### *Structure and composition*

Factors that affect the composition of phosphate coatings are type and amount of accelerator, application method (spray or dip) and presence of additional metal ions [8]. Energy-dispersive X-ray spectroscopy and X-ray diffraction are typically used to examine the structure and chemical makeup of Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> coatings. According to X-ray diffraction research, hopeite makes up most Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> coatings. Numerous experimental techniques, such electron spin resonance, X-ray fluorescence, scanning electron microscopy, Auger electron, X-ray photoelectron and Fourier transform infrared spectroscopy are used in phosphate coatings [20].

#### *Coating thickness and weight*

One of the most important factors in the coating choice is the thickness of the deposit that phosphating bath will produce. Although, for practical purposes, the thickness is typically measured in terms of weight per unit area (typically as g/m<sup>2</sup> or mg/ft<sup>2</sup>), which is referred to as coating weight, phosphate coatings can range from 1 to 50 microns. The difficulty in measuring coating thickness, which is exacerbated by the unevenness of the substrate and of the coating, is the reason coating weight is being considered as a preferred measurement instead of thickness. The coating weight can be calculated as in Eq. (7).

$$W = \frac{W_1 - W_2}{S} \quad (7)$$

where W is weight of phosphate coating (g/m<sup>2</sup>), S is substrate area (m<sup>2</sup>), and W<sub>1</sub> and W<sub>2</sub> are the samples' weight (g) after and before phosphating, respectively.

#### ***Coating porosity***

It is widely acknowledged that porosity decreases as phosphate coating thickness rises. Porosity is influenced by the kind of phosphate solution used, the length of the treatment procedure, Fe content in the bath and the coating's chemical composition [21].

**Adsorption mechanism of  $Zn_3(PO_4)_2$  on metal**

Adsorption is also known as the buildup of molecular species onto a solid surface. An adsorption isotherm, which explains an equilibrium relationship between the fluid concentration and the amount of the substance that is adsorbed at constant temperature, is used to analyze the degree of surfactant adsorption [22-23].

Interactions between adsorbate and adsorbent as well as adsorption mechanism are revealed by an adsorption isotherm. To develop an adsorption isotherm that can be mathematically modeled, a series of static adsorption tests can be performed on the liquid–solid interface for various concentrations of surfactants [24]. Langmuir has discovered the homogeneous monolayer of adsorption. Aside from Langmuir's isotherm, other ones are Henry's, Freundlich' and Redlich-Peterson's.

**Langmuir's isotherm**

Langmuir's isotherm can be considered for establishing the relationship between amount of adsorbed phosphate and adsorbent [25]. It can be written as Eq. (8).

$$\frac{C_{ads}}{\theta} = \frac{1}{K_{ads}} + C_{ads} \quad (8)$$

where  $C_{ads}$  is adsorbate concentration on the metal surface and  $K_{ads}$  is adsorption constant.

**Freundlich's isotherm**

Freundlich's adsorption isotherm is based on the adsorbate's multilayer adsorption. However, it does not apply to all isotherms. It can be implemented for multi-layer adsorption data onto a heterogeneous surface [26], and it mathematically represented as in Eq. (9).

$$\log \theta = \log K_{ads} + \frac{1}{n} \log C_{ads} \quad (9)$$

That is, a plot of  $\log \theta$  against  $\log C_{ads}$  gives a slope of  $\frac{1}{n}$  and an intercept of  $\log K_{ads}$  (in L/mg).

**Thermodynamics parameters of  $Zn_3(PO_4)_2$  coating adsorption process**

Thermodynamic parameters, such as  $K_{ads}$ , change in entropy ( $\Delta S$ - kJ/kmol), change in Gibbs free energy ( $\Delta G$ - kJ/kmol) and adsorption heat or enthalpy changes ( $\Delta H$ - kJ/kmol), can be computed by Eqs. (10-12), to further analyze the adsorption mechanism of an adsorbate [27].

$$\Delta G = -RT \ln K \quad (10)$$

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

where R is gas constant (8.314 J/mol/K), T is absolute temperature (K) and k is equilibrium constant in the adsorption process.

If  $\Delta G$  is negative across all temperatures, this indicates that the adsorption process is spontaneous. On the other hand, positive and negative  $\Delta H$  indicate endothermic

and exothermic processes, respectively.  $\Delta S$  negative values reveal a decreasing randomness during adsorption [28-29]. For the coating process, it is expected that calculated  $K_{ads}$  is positive,  $\Delta G$  is negative,  $\Delta H$  is positive and  $\Delta s$  is negative.

#### ***Mass transfer coefficient of the adsorbent on the metal during phosphating***

Mass transfer coefficient of coating material ( $k_f$ ) can be determined. This kinetic parameter can be employed for assessing the coating's effectiveness. It reveals the amount of coating material that can be adsorbed onto a given area of the metal surface in a particular time [6]. Eq. (13) can be used to calculate  $k_f$ . Thus, a plot of  $\frac{dc}{dt}$  against  $(c - c_s)$  will give a slope of  $\frac{3k_f}{r_p}$ , from which  $k_f$  can be assessed.

$$-\frac{dc}{dt} = \frac{3k_f(c-c_s)}{r_p} \quad (13)$$

where  $dc/dt$  is change rate of adsorbent concentration in the bulk solution over time,  $k_f$  is mass transfer coefficient ( $\text{kg}/\text{m}^2/\text{s}$ ),  $r_p$  is particle size (m),  $C$  is adsorbent concentration in the bulk solution ( $\text{kg}/\text{m}^3$ ) and  $C_s$  is adsorbent concentration on the external surface ( $\text{kg}/\text{m}^3$ ).

#### ***Some industrial applications of phosphating***

Some industrial applications of phosphating are: corrosion control, especially when combined with other films such as polymer films; paint based and/or other organic coatings; help in cold forming of steel such as wire drawing; enhancement of characteristics that cause friction, including friction coefficient, wear resistance, break-in and anti-galling; metallurgical production technology, as these coatings are resistant to wetting from molten metal; on the plates of a transformer, rotor, and stator, it can be used to create an insulating coating.

#### **Conclusion**

Since corrosion has a serious damaging effect on metal industries, the importance of studying on how to prevent or reduce these effects cannot be overemphasized. Metal surface coating is one effective way of preventing corrosion. In this review, chemical conversion coating techniques, types of phosphating and limitations, components, detailed process, adsorption mechanism onto the metal surface, thermodynamic and kinetic properties, and applications of  $\text{Zn}_3(\text{PO}_4)_2$  were considered.

#### **Conflict of interest**

The authors declare that there is no conflict of interest.

#### **Authors' contributions**

**A. A. Ayodeji:** conceptualization; supervision; methodology; writing. **E. E. Alagbe:** supervision; validation; review and editing. **C. Ogbuigbo:** resources; review and editing. **G. A. Agbeyegbe:** conceptualization; resources; investigation; writing.



## Abbreviations

**FePO<sub>4</sub>**: iron phosphate

**H<sub>3</sub>PO<sub>4</sub>**: phosphoric acid

**k<sub>f</sub>**: mass transfer coefficient of the coating material

**Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>**: manganese phosphate

**Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>**: zinc phosphate

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