Progress in Zinc Phosphate Conversion Coatings: A Review

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Abstract— Phosphating is one of the most widely used surface treatments of ferrous and non-ferrous materials due to its low-cost, easy production, good corrosion resistance and good adhesion with paint. Many researchers have tried to explore the different applications of the phosphating processes in various fields including automobile and aerospace. Recently, the zinc phosphate conversion coatings on magnesium alloys and aluminium alloys and the role of nano structured materials on the development and corrosion resistance of zinc phosphate coatings have been intensively studied. This paper reviews the state-of-the-art of phosphate conversion coatings on materials, in terms of past and present developments in the process of phosphatization, coating characteristics, evaluation of coatings, evolution of nano coatings and environmental impact.

Keywords— phosphating, corrosion, electrochemical studies, porosity.

I. INTRODUCTION

Metals are inevitable in our day to day life. Though efforts to find alternatives and replacements have been successful to a certain extent, metals still play a major role in the manufacture and construction and would be so for many more years to come. Besides several useful properties like strength, workability, low-cost and ability to be recycled, the metals have a major disadvantage in that they show a strong tendency to revert to their oxide form at the first available opportunity, i.e., they tend to corrode.

1.1 CORROSION- A BRIEF:

Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. The type of metal and the environmental conditions (particularly what gases that are in contact with the metal) determine the form and rate of deterioration. The World Corrosion Organization estimates the global cost of corrosion to be roughly US$ 2.2 trillion annually, and that a large portion of this - as much as 25% - could be eliminated by applying simple, well-understood prevention techniques. Corrosion prevention should not, however, be considered solely a financial issue, but also one of health and safety.

Corrosion can be prevented in the following ways:

Modification of the metal by alloying and/or surface modification; Modification of the environment by the use of inhibitors; and Change of metal/environment potential by cathodic or anodic protection. The most common method of corrosion protection involves surface modification or bulk alloying. Surface modification can be effected by physical or chemical processes. The chief function of surface modification is to provide an effective barrier against the corrosive environment. This can be achieved by several methods. Of all these, control of corrosion through the use of chemical conversion coatings, is the most cost effective method and used in a wider range of applications [1-6].

II. CHEMICAL CONVERSION COATINGS

Conversion coatings are produced by chemical or electrochemical treatment of a metal surface to produce a protective film, which is less reactive in aggressive environments than the original metal surface. There are a number of different types of conversion coatings, including chromate conversion coatings, phosphate-permanganate conversion coatings, and fluorozirconate conversion coatings. The conventional conversion coatings are based on treatment solutions containing chromium compounds that have been shown to be highly toxic and carcinogenic. Phosphating is one of the most widely used surface treatments of steels and aluminum due to its low-cost, easy mass production, good corrosion resistance and good adhesion with paint. Phosphate conversion coatings have been regarded as one of the suitable alternatives to chromate conversion coatings due to their low toxicity and appropriate properties. Phosphate conversion coatings on steels are classified into five types: zinc system, zinc calcium system, manganese system, manganese iron system and iron system coating [7-10]. In this review our focus will be on Phosphate coatings, especially Zinc Phosphating.
III. ZINC PHOSPHATING

Zinc phosphating (ZPO) is a conversion coating treatment that has been used for many years in the industry as a surface preparation for paint coating to increase adhesion and corrosion resistance [4–8]. Due to its economy, ease of formation, good corrosion protection and adhesion, zinc phosphating is widely used in many fields of industry such as automobile and domestic appliances [9,10].

3.1. Phosphating Process

Due to the advancement in Science and Technology and the resultant exponential growth in automobiles and domestic appliances, phosphate coatings for protecting steel surfaces have gained prominence since the turn of the century. The first reliable record of phosphate coatings applied to prevent rusting of iron and steel is a British patent of 1869 granted to Ross [11]. In the method used by him, red hot iron articles were plunged into the phosphoric acid to prevent them from rusting. Some of the developments in improving the quality of phosphating in the last 30 years are, [4] use of low temperature phosphating baths to overcome the energy crisis; use of low zinc technology; use of special additives in the phosphating bath; use of more than one heavy metal ions in existing composition—particularly tri-cation phosphating; etc.

3.2. Chemical Aspects of Phosphating

Conventional phosphating baths consist of dilute phosphoric acid based solutions of one or more alkali metal/heavy metal ions [12–15]. These baths essentially contain free phosphoric acid and primary phosphates of the metal ions. When a mild steel substrate is introduced into the phosphating solution, a topochemical reaction takes place, during which the metal dissolution is initiated at the micro-anodic sites on the substrate by the free phosphoric acid present in the bath. Hydrogen evolution occurs at the micro-cathodic sites.

\[
Fe + 2H_3PO_4 \rightarrow Fe(H_2PO_4)_2 + H_2 \uparrow
\]

The formation of soluble primary phosphate leads to the subsequent depletion of free phosphoric acid concentration in the bath which results in the rise of pH at the metal-solution interface. This change in pH alters the hydrolytic equilibrium that exists between the soluble primary phosphates and the insoluble tertiary phosphates of the heavy metal ions present in the phosphating bath resulting in a rapid conversion and deposition of insoluble heavy metal tertiary phosphate[12–15]. In a zinc phosphating bath, these equilibria may be represented as follows:

\[
Zn(H_2PO_4)_2 \leftrightarrow ZnHPO_4 + H_3PO_4
\]

\[
3ZnHPO_4 \leftrightarrow Zn_3(PO_4)_2 + 3H_2PO_4
\]

A certain amount of free phosphoric acid must be present to repress the hydrolysis and to keep the bath stable for effective deposition of phosphate at the cathodic sites. Shift in equilibrium between the primary and tertiary phosphates is also affected by the temperature of the bath. Tertiary phosphates precipitate readily at higher temperatures in a shorter time. Hence, for phosphating baths operated at higher temperatures, more amount of phosphoric acid is needed. On the contrary, in the case of low temperature phosphating baths, there is a possibility of increase in acidity during continuous operation [16] and is normally neutralized by the addition of carbonate of the coating metal (zinc carbonate in zinc phosphating bath). The operating temperature and concentration of the bath constituents decide the free phosphoric acid content which is required to maintain the equilibrium condition. Too much of phosphoric acid leads to excessive metal loss and delays the coating formation.

3.3 Acceleration of phosphating

Generally, phosphating process is slow due to the polarization caused by the hydrogen evolution reaction at the cathode. Acceleration is needed to speed up the process. The importance of acceleration of the phosphating process was felt way back in the 19th century and its development has gained rapid momentum with the advent of the Bonderite process in 1929. Recently, Sankara Narayanam et al [17] have made an overview on the acceleration of the phosphating process and justified its role to reduce process time. The hunting demand to reduce process time has led to the development of different modes of acceleration of the phosphating process. The modes of acceleration can be broadly classified as:

3.3.1 Chemical Acceleration

Oxidizing substances [18, 19] and metals more noble than iron such as Cu, Ni etc [19] form an important class of chemical accelerators. They accelerate the phosphating process through different mechanisms. Oxidizing agents depolarize the cathodic half cell reaction by preventing the accumulation of hydrogen at the cathodic sites, whereas noble metal ions promote metal dissolution by providing low over-potential cathode sites by their deposition [20]. Instead of mere promotion of metal dissolution, acceleration through depolarization is preferred. Because of this reason, oxidizing agents have found wide spread use than metals. Moreover, they prevent the excessive build up of iron in the bath, which is detrimental to good coating formation [15]. Oxidizing agents such as NO₃⁻, NO₂⁻, ClO₃⁻, C₆H₅(NO₂)(SO₃)Na (sodium metanitro benzene sulphonate-SMBS), C₃H₇SO₃Na (sodium dodecyl sulfate - SDS) or a mixture of them, have an influence on the depolarization of hydrogen evolution reaction by consuming the hydrogen ions at the cathodic sites [21–24]. If NO₃⁻ and NO₂⁻ ions are present in the zinc phosphating bath, nitrate
ion is reduced to nitrite ion which results in an increase of the local pH on the metal surface and deposition of ZPO takes place on the metal surface [20]. Fluorides such as NaF, HF were normally added as an activator in zinc phosphate coating solutions [20].

3.4.1 Cleaning

Before any process of metallic coating is applied to a metal substrate it is essential that the surface be in a suitable condition to receive the coating. Many coating failures are attributed to the poor metal surface preparation [29]. An ideal cleaning agent is the one, which is capable of removing all the contaminants from the metal surface, and prevents their re-deposition or the formation of other detrimental reaction products [30]. A variety of methods such as solvent de-greasing, sand blasting, vapour de-greasing, alkaline cleaning and pickling have also been used to achieve this.

3.4.2 Pre-Rinsing

The pickled panels are rinsed thoroughly in deionized water to remove the chemicals present on it after pickling [30].

3.4.3 Surface Activation

The ZPO coating crystal size and the coating weight can be controlled by this surface activation stage. Modern surface activation chemicals are weakly alkaline colloidal dispersion of titanium complex. This treatment leads to the formation of large number of finer crystallites of titanium compound on the metal surface which act as crystal nuclei for the growth of fine zinc phosphate crystals during the phosphating stage. Greater is the number of nucleating centres on the surface, more will be the inter-crystalline collisions and consequently finer will be the crystals and more compact will be the phosphate coating and better will be the paint adhesion and corrosion resistance of the phosphated and painted system [31,32]. The efficacy of surface activation bath is critically dependent upon: 1) pH of the bath and 2) The concentration of titanium. Yoshihara et al.[33] prescribed that the ideal pH of the activation bath should be in the range of 8.5 to 9.5 and Ti concentration should be minimum 10 ppm.

3.4.4 Phosphating

After cleaning the metal substrate, it is then subjected to phosphating, which causes the formation of an insoluble, corrosion resistant phosphate layer on the surface of the substrate. The phosphating solution is based on phosphoric acid and contains acid metal salts such as zinc, manganese and iron [12-15]. Based on the nature of the metal ion constituting the major component of the phosphating solution and also the minimum weight of the coating produced on unit area of the surface (grams per square metre or milligrams per square foot), these compositions are classified as zinc, manganese and iron phosphating baths. In India, phosphate coatings are covered by Indian Standard Specification IS:3618:1966 and Defence Specification WPN/GFN/3 [15]. Phosphating can be effectively performed on both ferrous and non-ferrous metals [4]. Among the ferrous metals, mild steels are most frequently used. Other type of steels which can be coated include galvanized steels, maraging steels and stainless steels. Zinc, aluminium, magnesium and cadmium [4] are some of the non-ferrous metals that can be phosphated. Phosphate coatings are normally applied to a surface either by spray or immersion processes and the choice of the appropriate method depends upon the size and shape of the substrate to be coated and based on the end use for which the coating is made. Operating temperatures of different phosphating solutions may range from 30-99°C [15] and processing time can be varied from a few seconds to several minutes. These parameters are determined by factors such as nature of the metal to be coated, thickness and weight of the coating required and
In order to obtain satisfactory phosphate coating, the bath parameters such as: (i) the free acid value (FA) which refers to the free H⁺ ions present in the phosphating solution (ii) total acid value (TA) which represents the total quantities of the coating forming substances; (iii) the ratio of free to total acid, expressed as the acid coefficient; (iv) accelerator content; (v) iron contents and (vi) other metallic and non-metallic constituents present, have to be strictly controlled within the optimum limits.

3.4.5 Rinsing after Phosphating

After phosphating, thorough rinsing with water is necessary to remove active soluble salts which would otherwise tend to promote blistering under a paint film. Care should be taken to ensure that the water supply itself is sufficiently free from harmful salts. Any phosphating chemicals carried over to the chromic acid rinse may contaminate the solution used. A rinse that is too warm may set the residual chemicals and cause them to adhere to the phosphate crystals, resulting in (a) rough coating, (b) whitish appearance of coating and (c) lower corrosion resistance. Generally overflow rinsing and spray rinsing are preferred [34].

3.4.6 Drying

After chromic acid rinsing, the parts must be dried before finishing. The conventional methods used are simple evaporation, forced drying by blowing air or by heating [35]. After drying, the phosphated panels are ready for application of further finishes such as paints, oils, varnishes etc.

3.5. Structure and Composition

Phosphate coatings consist of crystals ranging from a few to about 100 micrometers in size. The roughness of the coating depends on the base metal, its pre-treatment, the composition of the phosphating bath and the operating conditions, and ranges from 0.5 to 40 μm. Various workers have reported a large number of different constituents of phosphate coatings.

Neuhaus and Gebhardt [36] have tabulated the main phases in baths of various phosphates (Table 1). The composition of phosphate coatings are influenced by a number of factors such as the method of application, the degree of agitation of the bath, bath chemistry, the type and quantity of accelerator and the presence of other metal ions. Chamberlain and Eisler [37] have found using radioactive tracers that the base layer was formed initially from the metal being attacked during the first few seconds of contact with the phosphating bath producing a very thin film. The film contains oxides and phosphates of the metal being treated. Ferrous phosphate is most likely to be present in the case of steel. The growth of phosphate coating is initiated by the formation of a sub crystalline layer on which crystalline layer of phosphates build up rapidly [38-40]. The number of crystals on which growth has occurred is essentially constant with time because nucleation and growth takes place only at a limited number of active sites. Machu et al. [41] have postulated that these active sites were the growth areas located predominantly at the grain boundaries of the steel [42]. Light and electron microscopic studies [41, 43] made on zinc phosphated steel, have shown that the formation and growth processes occur at three stages. The stages are (i) formation of randomly oriented crystals on the surface and their lateral growth, (ii) nucleation and growth of several crystals on the upper surface of the original crystals in the vertical direction and (iii) spreading of thin layer of zinc phosphate from the base of the original crystals. Neuhaus et al. [36] have reported from the XRD analysis that phosphophyllite Zn₉Fe₃(PO₄)₉·4H₂O and hopeite, Zn₉(PO₄)₉·4H₂O are the essential constituents of zinc phosphate coatings on ferrous substrate, substantiated by others [44,45].

### Table 1 Phase constituents of phosphate coatings on Fe, Zn and Al

<table>
<thead>
<tr>
<th>Metal in the bath</th>
<th>Substrate</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe₉(H₂PO₄)₄·8H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
<td>AlPO₄</td>
</tr>
<tr>
<td></td>
<td>FePO₄·2H₂O</td>
<td>Zn₂FePO₄·4H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FeH₃(PO₄)₉·4H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>(Mn₂Fe₃)₉(H₂PO₄)₉·4H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
<td>Mn₃H₃(PO₄)₉·4H₂O</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn₉Fe₃(PO₄)₉·4H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
<td></td>
</tr>
<tr>
<td>ZnCa</td>
<td>Zn₂Fe₃(PO₄)₉·4H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn₂Ca(PO₄)₉·2H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
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<tr>
<td></td>
<td>Zn₉PO₄·2H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
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<td>Zn₉(PO₄)₉·4H₂O</td>
<td>Zn₉(PO₄)₉·4H₂O</td>
<td></td>
</tr>
</tbody>
</table>

3.6. Factors Influencing Coating Properties

3.6.1. Nature of the Substrate

The major factors which determine the nature and quality of the coatings obtained are the nature of the metal substrate being coated, the composition, concentration and temperature of the phosphating solution. Other decisive factors include the condition of the metal surface before phosphating and the post passivation or sealing step. The effect of the base metal on coating formation was studied by Kozlowski [46]. Da Pos and Tosto [47] have presented a thorough review on the conditions which influence the phosphating process.
3.6.2. Phosphating Parameters

The formulation of the phosphating solution determines the nature of the coatings formed. Higher concentrations of heavy metal ions in accelerated phosphating solutions yield coatings of better protective value [48]. The acidity of the bath, i.e., the free acid value (FA), total acid value (TA) and their ratio (FA:TA) should be maintained at the required optimum level to obtain coatings of improved quality. According to El-Mallah et al [49], reducing the difference between the initial pH and final pH (pH at which the consumption of all the free phosphoric acid completes) leads to the acceleration of the phosphating process. In producing such an effect the heavy metals and reducing agents such as hydrazine, potassium borohydride were tried. Several additives have been tried to maintain the pH of the phosphating baths. In this respect, organic acids and their salts have proved their ability to buffer the pH of an iron phosphating bath made up with hard water [50]. It has been shown that the compact and dense phosphate coating were formed in the phosphating bath with pH 2.75. Polarization measurement also showed that the highest increase in the corrosion resistance was obtained when the pH of the phosphating was 2.75,[51]. The accelerator concentration also plays an important role in phosphating. Though increase in accelerator concentration favours better coating formation, too high concentration may cause passivation of metal surface and inhibit the growth [52]. The concentration of the accelerator content should be optimized when additives such as surface active agents are added [53]. Even though a small quantity of iron salts favour phosphate precipitation (break-in of the bath), increase in the quantity affects the corrosion performance largely [54]. Other Additives such as ethylene diamine tetra acetic acid (EDTA), nitrilo triacetic acid (NTA), diethylene triamine penta acetic acid (DTPA), gluconic acid, polycarboxy o-amino acid, and ethanalamine are commonly used as a chelating agent and corrosion inhibitor [5,56].

The addition of calcium ions in a zinc phosphating bath has resulted in a considerable change in the crystal structure, grain size and corrosion resistance of phosphate coatings. It leads to the change in the structure of the zinc phosphate coating from the phosphohydrate-hopeite to schlozite-hopeite [57]. This kind of calcium-modified zinc phosphating [58] results into reduction in grain size (25m to 4m) and the improvement in the compactness of the coating and corrosion resistance. Similarly, the inclusion of manganese and nickel ions in the zinc phosphating bath proves to be useful in refining the crystal size and improving the corrosion resistance of the resultant phosphate coating[59]. The inclusion of manganese and nickel ions modify the hopeite deposits equivalent to phosphohydrate to have better thermal and chemical stabilities [60]. This type of phosphating is classified as nickel and manganese modified zinc phosphating [58]. Moreover, such modifications have led to the development if tri-cation phosphating baths consisting of zinc, manganese and nickel ions which explored its potential utility to phosphate aluminium, steel and galvanized steel using the same formulation [61 - 63].

Besides these major types of modifications, phosphating baths have experienced a variety of additives incorporated in the bath intended for a specific purpose. Each additive added to the phosphating bath has its own influence on the phosphatability of steel depending upon the operating conditions [64-68]. Sankara Narayanan et al [69] have classified the types of special additives used in phosphating and the purpose of their use. The favourable condition and the precautions in using these additives were recommended in the respective documents. Operating temperature of phosphating baths plays a significant role in phosphating. Insufficient reach of operating temperature do not favour the precipitation of insoluble tertiary phosphate from soluble primary phosphate. However, over heating of the baths above the recommended operating temperature causes an early conversion of the primary phosphate to tertiary phosphate before the metal has been treated and as a result increases the free acidity of the bath, which consequently delays the precipitation of the phosphate coating. The decisive role of overheating the phosphating baths and the possible ways of eliminating the difficulties encountered due to this problem was discussed by Sankara Narayanan et al [70]. It has been confirmed that the coverage of the phosphate layer increased as the temperature of phosphating bath increased to 55 °C. At high temperature (65 °C and 75 °C) the deposition coverage decreased. Electrochemical results in aerated 3.5% NaCl also showed that the corrosion current density of the phosphated substrates was minimum (2.77 μA/cm2) when the phosphating temperature reached to 55 °C[71]. Recently, studies have been carried out in electrochemical phosphating to produce phosphate coatings richer in a particular phase by selecting an appropriate applied potential [72]. Electrochemical method of phosphating yields a heavy coating weight [73,74]. But there are difficulties encountered in adding ‘electrics’ to the existing process plants in electrochemical phosphating. Mechanical vibration of steel during phosphating produces fine-grained phosphate coating. However, the amount of coating formed is found to be inversely proportional to the frequency of vibration [75]. Ultrasonically induced cavitation produces a greater number of active centres, which results in a high rate of nucleation. This leads to a uniform fine-grained phosphate coating with low porosity [76,77].

3.7. Defects in Coatings and Remedies

Phosphated parts with low corrosion resistance, stained coating with variable corrosion resistance and coatings covered with a loose white powdery deposits are some of the commonly encountered defects in phosphated parts. These defects may be due to unsuitable operating conditions, too highly oxidizing an accelerator,
insufficient care in degreasing and cleaning, incorrect acid coefficient, excessive sludge formation and faults in post treatment. Presence of certain metallic impurities like aluminium, antimony, tin and lead compounds, presence of chloride ions, incorrect acid coefficient and incorrect bath parameters and operating conditions may result in low corrosion resistance. Stained coatings may be formed due to improper cleaning and degreasing. Over heating of the phosphating bath, make-up during processing, heavy sludging and sludge suspended in the bath leads to the formation of coatings with a loose powdery deposit. Good quality coatings are resulted from proper cleaning and degreasing of the work surface, correct maintenance of work surface to solution volume ratio, control of bath parameters and operating conditions and by avoiding overheating and excessive sludge formation. Some of the drawbacks observed in using conventional phosphating formulations are long processing time, sludge formation and less process flexibility. These drawbacks have been largely overcome effectively through the introduction of special additives [78]. Each of these additives has been used to solve a specific need of the phosphating industry. However, a single additive, which could satisfy a variety of needs is expected by the phosphating industries viz., improved corrosion resistance, adhesion, formation of good coatings in low treatment time with minimum sludge and scale formation and suitable for a wide range of finishes applied over phosphated articles, is lacking.

3.8. Recent Developments

It is evident from the above that the existing phosphating process have to undergo several modifications to achieve better results. With the predominant purpose of solving the problems faced due to energy crisis, it is proposed to formulate a phosphating bath capable of operating at low temperature. It is well known that the accelerator plays a very important role in the treatment temperature and process time decrease in the phosphating process [79,80]. Feng Fang et al.[81] developed a modified low – temperature Zinc phosphating process on the surface of high – carbon steel, accelerated by an eco – friendly hydroxylamine sulfate (HAS) instead of common accelerator nitrite. The Phosphate coating consists of Zn_3(PO_4}_2.4H_2O and Zn_3Fe(PO_4}_2.4H_2O phases. It was established that the coating is thinner and more compact due to the addition of HAS. The crystal size markedly decreased from 100μm to 50 μm and the content of Zn_3Fe(PO_4}_2.4H_2O increases from about 30% to 44% due to the addition of HAS (81).

The low temperature phosphating processes have become more significant today due to economical reasons. However the limitation of low temperature processes is that these processes involve greater consumption of chemicals and longer process time, besides limited process flexibility. Arthanareeswari et al. [81-84] investigated the effects of galvanic coupling of mild steel with various cathode materials such as titanium, copper, brass, nickel and stainless steel on the phosphatability and corrosion resistance. It is reported that the extent of metal dissolution and of coating formation are higher for mild steel substrates phosphated under galvanically coupled condition than without coupling. It is further established that the galvanic coupling of mild steel with metals that are nobler than steel during low temperature phosphating is beneficial in accelerating the rate of coating formation and producing uniform, less porous and higher weight coatings [85].

3.8.1 Zinc phosphate coatings on aluminium alloys

Phosphating is a well-known surface pretreatment process for both ferrous and nonferrous metals. There were a few reports of zinc phosphate coatings on aluminum alloys recently. Akhtar et al. [86–88] studied the effect of pH and role of Ni^{2+} on zinc phosphating of 2024-Al alloy. Sun et al. [89] investigated the effect of copper on zinc phosphate coating on aluminum surfaces. The influence of copper on coating morphology was emphasized. Phosphating baths containing mainly ZnO, H_3PO_4 and NaF was employed to obtain zinc phosphate coating on aluminum alloy and Ni (NO_3)_2 was used as the accelerating agent [87]. It has been shown that the addition of metal salts in the phosphating bath can greatly influence the microstructure of zinc phosphate coating and made the coating denser and finer [90]. Regarding the application of rare earth elements on the surface treatment of aluminum alloy, Bethencourt et al. [91] observed, from weight loss and polarization results, that lanthanum, cerium and samarium chlorides are effective corrosion inhibitors of AA5083 Al–Mg alloy in 3.5% NaCl solution. Arnott et al. [92] investigated the corrosion inhibition behavior of different rare earth chlorides on AA7075 aluminum alloy in 3.5% NaCl solution. Tran et al. [93] studied the corrosion behavior of steel in the presence of Y(III) salts in 3% NaCl solution.

The phosphating process on aluminum alloy involves the following reactions [88,94]:

\[ Al \rightarrow Al^{3+} + 3e^- \] (anodic) \hspace{1cm} (1)

\[ 2H^+ + 2e^- \rightarrow H_2 \uparrow \] (cathodic) \hspace{1cm} (2)

Insoluble tertiary phosphate is formed by the following reactions:

\[ H_3PO_4 + H_2PO_4^- \leftrightarrow 2H^+ + HPO_4^{2-} \leftrightarrow 3H^+ + PO_4^{3-} \] (3)

\[ 3Zn^{2+} + 2PO_4^{3-} \rightarrow Zn_3(PO_4)_2 \downarrow \] (4)

Here, Zn_3 (PO_4)_2 4H_2O is the main ingredient of the phosphate coating. Reactions(3) and (4) progress continuously until the nucleation and growth of zinc phosphate crystals to form the integrated phosphate coating and all the micro anodic sites are covered.
Because of the difference in the standard potential of zinc (−0.76 V) and aluminum (−1.66 V), Al on aluminum alloy surface dissolved in phosphating bath to give out electrons, which reduced some Zn²⁺ near the surface to metallic Zn deposited on the surface on the micro cathodic sites and become the composition of the phosphate coating [94]:

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \]

It is reported that when Y₂O₃ was used as an accelerator instead of nitrite a well-crystallized zinc phosphate coating was formed on 6061-Al alloy in a phosphating bath containing ZnO, H₂PO₄, NaF and Y₂O₃. The phosphate coating formed is composed of hopeite and metallic zinc. The formation of phosphate coating is strongly influenced by the presence of Y₂O₃ in the phosphating bath. The addition of Y₂O₃ to the phosphating bath not only decreases the size of the crystals and allows the formation of a more compact phosphate coating. The OCP shows that the phosphating process in the phosphating bath with 20 mgL⁻¹ Y₂O₃ needs shorter time at which the steady potential value is achieved [95].

### 3.8.2 Zinc phosphate coatings on magnesium alloys

There were some reports on the phosphating processes of magnesium alloys [96-98]. It was established by NIU Li–yuan [99] that finer cathodic phosphate coatings are formed on the AZ91D magnesium alloy in the phosphating bath at 0.2 -0.5 A/dm². The optimal bath compositions are: 15.5–17.8 g/L of 85% phosphoric acid; 2.5–3.9 g/L of zinc oxide; 1.5–1.8 g/L of sodium fluoride; 0.03–0.05 g/L of sodium dodecylsulfate. Zn₃(PO₄)₂·4H₂O, AlPO₃, Mg₂Zn₃(PO₄)₂ and zinc particles are the main constituents of the cathodic phosphate coating. The average grain size of the metallic zinc in the film is about 28.2 nm and the content of the metallic Zn particles in the coating decreases with the increase of the coating thickness. Ethanolamine as an additive was beneficial to the corrosion resistance of the zinc phosphate conversion coatings on magnesium alloy by refining the microstructure of the phosphate crystal layer[24]. Both nitrates and nitrites were used as accelerators for ZPO on magnesium alloys. Since nitrite is a carcinogen, it was avoided and other accelerators such as chlorate(NaClO₃)[100], sodium metatungsten naphtenate[101] and molybdate [102] were used as accelerating agents for phosphatization to replace nitrite to speed up the process and to reduce environmental pollution.

Adhesion and corrosion resistance were found to increase by the addition of nickel [103] and calcium [104] in the zinc phosphating baths.

Both Zn²⁺ and Ca²⁺ can be incorporated into the phosphate coatings when (Ca(NO₃)₂) was added to a zinc phosphating bath on Mg alloys, which then exhibit better corrosion resistance than zinc phosphate coatings alone [104]. The mechanism of ZPO coating formation on magnesium alloys can be explained by the following reactions: when magnesium alloy is immersed in phosphating solution, magnesium dissolves at micro anodes and hydrogen is evolved at micro cathodes (1,2),

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (1) \]
\[ 2H^+ + 2e^- \rightarrow H_2 \quad (2) \]

The presence of an accelerator like nitrite ions increase the pH of the phosphating solution by the following reaction (3):

\[ \text{NO}_3^- + 2H^+ + 2e^- \rightarrow \text{NO}_2^- + H_2O \quad (3) \]

At pH 3 ± 0.2, magnesium can precipitate as Mg₃(PO₄)₂ on the magnesium alloy (4).

\[ 3\text{Mg} + 2\text{H}_2\text{PO}_4^- \rightarrow \text{Mg}_3(\text{PO}_4)_2 + 3\text{H}_2 \quad (4) \]

Hopeite phase on magnesium alloy is formed by the following reaction (5):

\[ 3\text{Zn}^{2+} + 2\text{H}_2\text{PO}_4^- \rightarrow 2\text{H}^+ + 4\text{H}_2\text{O} + 6e^- \rightarrow \text{Zn}_3(\text{PO}_4)_2·4\text{H}_2\text{O} + 3\text{H}_2 \quad (5) \]

The overall phosphating reaction can be described as follows (6):

\[ 3\text{Mg} + 3\text{Zn}^{2+} + 4\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} \rightarrow \text{Zn}_3(\text{PO}_4)_2·4\text{H}_2\text{O} + 3\text{H}_2 + \text{Mg}_3(\text{PO}_4)_2 + 2\text{H}^+ \quad (6) \]

The formation of MgZn₃(PO₄)₂ is explained by reaction (7):

\[ \text{Mg}^{2+} + 2\text{Zn}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{MgZn}_3(\text{PO}_4)_2 \quad (7) \]

Presence of fluoride ions in the phosphating bath might affect the coating properties by the following reactions (8,9) [104]:

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \quad (8) \]
\[ \text{Mg(OH)}_2 + 2\text{H}^+ + 2\text{F}^- \rightarrow \text{MgF}_2 + 2\text{H}_2\text{O} \quad (9) \]

The presence of zinc and zinc oxide can be explained as follows (10,11,12) [104]:

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad (10) \]
\[ \text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{H}_2 \quad (11) \]
\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (12) \]

In the presence of calcium ions in the phosphating solution, the following reactions take place (13,14) [104]:

\[ \text{Zn}^{2+} + 2\text{Ca}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{Ca}_2(\text{OH})_2 \quad (13) \]
\[ \text{Zn}^{2+} + 2\text{H}_2\text{O} + \text{Ca}_2(\text{OH})_2 \rightarrow \text{Zn(OH)}_2 + \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} \quad (14) \]
3.8.3 Evolution of Nano Coatings

Recently, nanostructure materials have attracted considerable interest due to their importance in fundamental researches and potential wide – ranging applications. The application of nanostructure materials injected an impetus into the conventional industries such as coatings, plastics and rubber [105]. In the coating industry, with the help of this kind of nanotechnology, the quality of coatings might be enhanced to be novel characteristics [105-107]. The nanoparticles can absorb the inhibitor ions during the preparation and then slowly release them in contact with moisture. In this way, they can prolong the release of the inhibitor ions and also decrease the negative effect of the inhibitor ions on the stability of the coatings [108]. Moreover, functional nancontainers can be fabricated by the sequential deposition of inhibitors with polyelectrolytes onto surface charged nanoparticles [109]. The nancontainers combine the advantages of corrosion inhibitors and nanoparticles in corrosion protection [110,111]. As the polyelectrolyte multilayer acts as a barrier between the inhibitors and the coating, stable and long term corrosion protection of metallic structures can be achieved.

In addition to the use of SiO\(_2\) as filters, catalysts, catalyst supports, absorbents and chromatographic agents [112-115], the effectiveness of nano SiO\(_2\) as environmental friendly accelerator as replacement for aggressive oxidants because of its stability and non liberation of harmful nitrogen oxides has been established. The influence of nano SiO\(_2\) on the morphology of the phosphate coatings was studied [116]. The weight of phosphate coatings increased linearly with the nano SiO\(_2\) content in the bath from 0 to 4 g/L, and the phosphate coatings formed in bath containing 3g/L of nano SiO\(_2\) showed the lowest roughness. The X – ray diffraction analysis showed that the main phases found in the phosphate coatings obtained in the baths were Zn\(_2\)(PO\(_4\))\(_2\).4H\(_2\)O (hopeite) and Zn\(_2\)Fe(PO\(_4\))\(_2\).4H\(_2\)O (phosphophyllite). The addition of nano – SiO\(_2\) could be propitious to form new crystal nucleation and alter the preferential orientation to control the size of the phosphate crystal clusters. The electrochemical characterization of the phosphate coatings deposited in the bath with nano – SiO\(_2\) was found to have better corrosion resistance compared to coatings deposited in the bath without nano – SiO\(_2\) [116].

Phosphate coating including zinc, iron and manganese are the most commonly used form for corrosion protection and primer for painting [117]. Recent efforts to enhance the corrosion resistance of phosphate coatings have mainly been focused on the pre- treatment methods before phosphating and the process technologies for phosphating [10,118-121]. The dissolution of zinc during the process of phosphating is a serious problem as it adversely affects the corrosion resistance characteristics of the overall coating.

It has been shown that addition of metal salts in the phosphating bath can greatly influence the microstructure of zinc phosphate coating and make the coatings denser and finer [122,123]. Addition of Mn\(^{2+}\) into the phosphating bath improves the corrosion resistance of zinc phosphate coatings on steel and zinc coated steel[124,125]. Also it has been reported that the addition of Ni\(^{2+}\) into the phosphating bath improve the corrosion resistance of zinc phosphate coatings on the 2024 Al alloy [118,126]. Generally metal oxides play a versatile and important role in heterogeneous catalysis, electrochemistry, gas sensors and corrosion wear protection [127,128]. TiO\(_2\) is an effective ceramic material having high stability and non toxicity. It is reported that incorporation of nano TiO\(_2\) in to the phosphating bath significantly reduced the number of pores and yielded thicker coatings [124]. The paintability of the coating was also better than the normal phosphate coating. Results from the electro chemical analysis revealed the better barrier protection characteristics and enhanced corrosion resistance of TiO\(_2\) incorporated phosphate coatings over the normal phosphate coatings [129]. Tamilselvi et al. recently reported the development of nano zinc phosphate coatings [130]. Nano crystalline zinc phosphate coatings were developed on mild steel surface using nano zinc oxide particles. Significant variation in the coating weight, morphology and corrosion resistance was observed as nano ZnO concentrations were varied from 0.25 -2g/L in the phosphating baths. The results showed that nano ZnO particles in the phosphating solution yielded phosphate coatings of higher coating weight, greater surface coverage and enhanced corrosion resistance than the normal zinc phosphate coatings (developed using normal ZnO particles in the phosphating baths). Better corrosion resistance was observed for coatings derived from phosphating bath containing 1.5g/L nano ZnO. The activation effect brought about by the nano ZnO reduces the amount of accelerator (NaNO\(_2\)) required for phosphating. The nano zinc phosphate coatings developed has comparable corrosion resistance to zinc phosphate coatings developed using galvanic coupling methods or by the coatings developed using electrochemical methods [131]. Fig.1 shows the SEM image of nano zinc phosphate coatings developed [130].The average grain size of the nano ZPO coating is between 30-40 nm. Fig.2 shows the TEM image of nano zinc phosphate coatings. Salt spray test (Fig.3) of nano coatings exhibited better corrosion resistance than normal coatings.
Fig. 1 SEM image of nano zinc phosphate coatings

Fig. 2 TEM image of nano zinc phosphate coatings

Fig. 3 The corrosion behaviour of (a) normal zinc phosphate coating, (b) nano zinc phosphate coating on mild steel specimens and subsequently finished with a paint coating (DFT: 50 µm) after subjecting them to salt spray test for 96 hours.

3.9 Characterization of Phosphate Coating

Methods to evaluate the quality of phosphate coatings involve the determination of its physical characteristics as well as the performance in corrosive environments. Kwiatkowski et al. [132] have reviewed the testing methods of phosphate coatings.

3.9.1 Evaluation of Physical Characteristics

3.9.1.1 Visual Inspection

Obvious defects such as bare patches and non-uniformity in phosphate coatings are readily visible to the naked eye. Phosphate films on steel may range in colour from light gray to dark gray, depending on the type of bath and the grade of steel substrate used.

3.9.1.2 Determination of Coating Thickness and Coating Weight

This is probably the most important single parameter used to characterize phosphate coatings. The local thickness of phosphate coatings on steel is usually determined by magnetic, electromagnetic and microscopic methods [12-15]. The average thickness is usually expressed in g/m² or mg/ft². The weight of coating per unit area i.e., the coating weight is determined by a destructive procedure in which the coating is dissolved from a test specimen in a suitable medium and the specimen weighed before and after stripping. The medium selected should of course be without attack on the basis metal, to avoid error. Concentrated hydrochloric acid containing 20g/l of antimony trioxide is usually used at room temperature for this purpose. Other solutions commonly used are 5% solution of chromic acid at room temperature and 20% sodium hydroxide at 90°C. The difference in weight (coating weight) is expressed as g/m².

3.9.1.3 Determination of Acid Resistance

It is calculated as the difference in weight per unit area of the panel before phosphating and after stripping off the coating; and is expressed in g/m².

3.9.1.4 Estimation of Porosity

Porosity of the phosphate coating can be estimated based on the measurement of the oxygen reduction current density when immersed in air – saturated sodium hydroxide solution (pH11). The current density values measured at – 550mV, where oxygen reduction is the dominant reaction at the uncoated areas, reveal the porosity of the coating [4].

The chemical (Ferroxyl indicator) method of estimation of porosity was based on the formation of blue spots (Prussian blue) on a filter paper dipped in potassium ferricyanide – sodium chloride - gelatin mixture when applied over the phosphated surface for one minute. The number of blue spots per sq.cm gives a measure of the porosity of the coating.

Although, both the electrochemical test and the Ferroxyl test are used in an industrial scale to assess the porosity of phosphated steel, the latter method is found to be qualitative and not very effective in distinguishing the porosities of panels phosphated using different baths. In contrast, the electrochemical method is far reliable besides its simplicity in operation and quicker measurements of the porosity. [133].

3.9.1.5 Determination of Thermal and Chemical Stabilities

The thermal stability of the coating is usually determined by calculating the percentage loss in weight when the phosphated panels were subjected to drying at 120 and 180°C. The Chemical stability is determined by calculating the percentage residual coating when immersed in alkaline media. Determination of alkaline stability is important as it determines the effectiveness of the phosphate coating as a base for cathodic
electrophoretic finishes. Immersion in sodium hydroxide solution is recommended to test the alkaline stability. Recently, Kwiatkowski et al [134] have recommended a borate buffer solution containing 0.01M EDTA as the medium to test the alkaline stability of the coating and proved its usefulness in predicting the same. A similar calculation of the percentage residual coating when subjected to immersion treatments in buffered solutions of varying pH from 2–14 can give an insight about the ability of the phosphate coatings to withstand different chemical aggressions and to prove their effectiveness in preventing the cosmetic corrosion [135].

### 3.9.1.6 Evaluation of Surface Morphology

Usually coatings morphology and crystal size are determined by Scanning Electron Microscopy (SEM) and the crystal phases are determined by X-ray Diffraction technique (XRD) and elemental analysis on the surface coating may be done by Energy Dispersive X-ray analysis (EDX).

#### 3.9.1.7 Adhesion Measurements

The standard laboratory method of estimation of adhesion is the peel off test, which involves the determination of extent of adhesion at scribed areas using a pressure sensitive adhesive tape. Usually adhesion in the dry state will be good since it mainly depends on the cohesive failure of the paint film. Wet adhesion is of prime importance and is usually determined after subjecting the painted panels to immersion treatment in deionized water at 45°C for 240 hours. Depending upon the extent of peeling, rating will be made between 0 and 5B as per ASTM D 3359-87 [136].

### 3.9.2 Evaluation Of Corrosion Resistance

#### 3.9.2.1 Preliminary Quality Control Tests

Preliminary investigation of coating quality for on-line monitoring mainly involves two empirical tests of which one involves inspection of rust spots after immersion in 3% sodium chloride solution for 5–30 minutes and the other concerns with the time taken for metallic copper deposition from a copper sulphate–sodium chloride–hydrochloric acid mixture.

#### 3.9.2.2 Laboratory Corrosion Resistance Tests

The most frequently used laboratory tests for evaluating the corrosion resistance of phosphate coatings include (i) immersion tests, (ii) salt spray (fog) test (iii) humidity test and (iv) A.R.E. salt droplet test.

##### 3.9.2.2.1 Immersion Test

This test consists of determining the time required for the first appearance of corrosion on the basis metal when immersed in 3% sodium chloride solution. The change in weight expressed as g/m² for every 24 hour period of immersion is also determined and correlated to the corrosion resistance of the coating.

#### 3.9.2.2.2 Salt Spray Test

This test consists of subjecting the phosphated and finished panels to a salt mist of 5% sodium chloride solution in a salt spray chamber for a specified length of time. The extent of spread of corrosion from a scribe made on the panel, rated after ASTM B 117-85 specifications, is a measure of the corrosion resistance of the phosphate coating [137].

The main value of salt spray test is in the evaluation of the effectiveness of phosphate coatings in restricting the spread of rust from scratches or other points of damage in paint film. This feature is of particular interest to the motor car industry, as vehicles are often exposed to marine atmospheres and to moisture and salt when the latter is used to disperse ice and frost from road surfaces in cold countries.

##### 3.9.2.2.3 Humidity Test

Humidity test is conducted to check the efficiency of the rinsing procedure. This test consists of subjecting the phosphated panels to highly humid conditions (90-95% relative humidity) at slightly elevated temperatures (42-48°C). Assessment of corrosion likely to be induced due to the porosity of the coating can be made. The extent of blistering of paints due to the presence of soluble salts on phosphated and finished panels when subjected for 1000 hours in the humidity chamber, is also related to its corrosion performance. This test indicates the presence of harmful water soluble mater of the paint film and is particularly valuable for showing contamination by finger marks.

##### 3.9.2.2.4 A.R.E. Salt droplet test

This test consists of the evaluation of corrosion resistance of the phosphated panels by determining the loss in weight after five days of exposure in humid condition inside a closed cabinet at room temperature with a single spray of synthetic sea water on each day [138].

### 3.9.3 Electrochemical Methods of Testing

The electrochemical methods for testing the phosphate coating mainly involve the anodic polarization studies in 0.6M ammonium nitrate [133,139] and AC impedance measurements in 3% sodium chloride solution [140,141].

The anodic polarization studies in 0.6M ammonium nitrate solution is based on the active-passive transition with applied potential. During anodic polarization in 0.6 M ammonium nitrate solution, at potentials more negative
than -0.33V, phosphated steel undergoes active
dissolution. Above -0.33V, the first passivation region
occurs due to the adsorption of hydroxide ions at the
electrode surface. The occurrence of the second active
region is due to the replacement of hydroxide ions by
phosphate ions available at the electrode/solution
interface. Replacement of the adsorbed phosphate ions by
nitrate causes the occurrence of the second passive region.
Hence it is clear that these active and passive regions are
the result of the competitive and potential-dependent
adsorption of anions at the electrode surface. It should be
noted here that the appearance of this second current
density maximum is specific to phosphated steel and it is
not observed for uncoated steel when tested under similar
conditions. Hence the value of the second current density
maximum can be used to evaluate the corrosion resistance
of different phosphate coatings [133,139].

AC impedance studies involve the measurement of the
charge transfer resistance (R\text{ct}) , the double layer
capacitance (C_{dl}) and the Warburg impedance (Z_{w}),
the parameters that constitute the proposed equivalent
electrical circuit model in correlation with the behaviour
of coated system in a corrosive environment. Literature
reports on the evaluation of phosphate coatings [4,142]
suggest that the corrosion behaviour of phosphate
coatings in contact with the corrosive medium (3.5%
NaCl) can be explained on the basis of a porous film
model since the electrolyte/coating-metal interface
approximates such a model. Accordingly, the phosphated
substrates are considered as partially blocked electrodes,
when come in contact with 3.5% NaCl solution. This
implies that the metal substrate is corroding in the same
way when protected in a much smaller area where
coverage is lacking. Since the capacitive and resistive
contributions vary directly and indirectly, respectively,
with respect to the area, based on these measured
parameters, predictions on the corrosion rate of different
phosphate coatings can be easily made. High values of
charge transfer resistance and a low value of double layer
capacitance signifies a coating of better performance. The
appearance of Warburg impedance helps in predicting
whether the process is diffusion controlled or not [4].

3.10. Environmental Impact

Several waste streams are generated by coating processes.
Solid waste includes empty coating containers, coating
sludge from overspray and equipment cleaning, spent
filters and abrasive materials, dry coating and cleaning
rags.

Phosphating sludge, in general, has 20 wt.% iron, 10 wt.%
zinc, 1-3 wt.% manganese, <1 wt.% nickel and 50-55
wt.% phosphate (composition on dry basis). Hence efforts
are focused on the recovery of zinc, iron and phosphate
for preparing phosphating solution and/or make-up feed.
Among the various methods proposed for reclaiming
phosphating sludge, pyrometallurgical processing –

reduction sintering processes, for recovering the metals
zinc, iron and nickel in addition to sodium phosphate; wet
chemical processing by leaching constituents with acids
and bases and reusing them in the preparation of
phosphating solutions; and digestion with mineral acids,
removal of constituents and their reuse are prevalent. The
use of phosphating sludge in the process of clinker
production is suggested as one of the possible mode of
reclamation of such waste by Caponero and Tenorio
[143]. Their study proves that an addition of up to 7.0% of
phosphating sludge to the raw cement meal of Portland
cement did not cause any damage to the clinkerization
process.

Liquid wastes include waste water from surface
preparation, overspray control or equipment cleaning,
off-specification or excess coating or surface preparation
materials, overspray, spills and spent cleaning solutions.
Onsite closed-loop recycling is becoming more popular
for spent solvents as disposal costs rise. Water-based
liquids are usually treated onsite prior to discharge to
publicly owned treatment systems.

VOC emissions are generated by all conventional coating
processes that use solvent-based coatings, requiring
control devices such as carbon adsorption units,
condensers or thermal catalytic oxidizers

IV. CONCLUSION

Due to liberalization of the economy in India, enormous
growth was seen in the Automobile and consumer
durables industry in the last decade or so. In these two
industries Phosphate conversion coatings played a vital
role. Hence this review attempts to outline the various
aspects of Phosphating. The numerous improvements
reported recently like Galvanic coupling, addition of
metal salts to the Phosphating bath etc., to enhance
corrosion and wear resistance are also brought out. The
emerging nano science is also considered and the reports
made on nano coatings are also discussed.

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