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Review Article

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Recent Advances in Phosphatization of Metals for Corrosion Protection

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Abstract

Corrosion of metals is a broad-based issue that has significant economic and ecological consequences. It is a surface treatment method that is popularized for its promising results in inhibiting corrosion and increasing the life span of metal components. The review paper provides an in-depth analysis of the phosphatization process, its mechanisms, and the resistance properties offered by coated metals. After thorough investigations, the impact on various metals, including steel, aluminum, and zinc of phosphating has been explored. The study further explored the influence of key factors such as composition, pH, temperature, and immersion time of the metal in chemical acid. Additionally, the paper also examines the interaction between the metal surface and the chemical solution of phosphoric acid in which it has been immersed which leads to the formation of a phosphate layer over the surface. The paper also discusses the effectiveness of different phosphate types such as zinc, iron, and manganese phosphates in providing corrosion resistance. Further the paper analyses the role of phosphate coatings in altering the surface properties, including adhesion, wettability, and microstructure, to enhance the metal's resistance to corrosive environments. Finally, this review summarizes the current challenges and future directions in phosphatization research. The findings of this research contribute to the development of efficient corrosion protection strategies, fostering advancements in the field of chemistry.

Keywords

Corrosion, Phosphatization, Immersion time, Adhesion, Wettability

Introduction

The deterioration or degradation of metals due to chemicals or moisture in the environment is one of the significant problems faced worldwide. The impact of corrosion is usually high as it affects the strategies in the industry [1]. A surface treatment method has been established called phosphatization, which is widely accepted and has a promising approach for corrosion prevention and protection of metals [2]. During this method, the metal forms a phosphate layer on its surface blocking the direct contact of the surface with moisture or any corrosive agents. It has other applications like paint adhesions, enhanced corrosion resistance and increased surface hardness. The application of phosphatization techniques could be seen in diverse industries, including the automotive, aerospace, construction, and marine sectors [3]. The two most common corrosion prevention strategies are bulk alloying and surface modification. Surface modification, on the other hand, is more prevalent and significantly less expensive than bulk alloying. These methods are widely used for metals like iron, manganese, zinc, etc. [4].

The technique of treating a metal surface to produce an insoluble phosphate coating that is contiguous, strongly adherent to the underlying metal, and much

more absorbent than the metal is referred to as the "phosphatization". The surface of the base metal integrates into the corrosion-resistant film because of the topochemical reaction that produces the coating. Phosphatization is preferred for the protection against metal corrosion because of its corrosion resistance, advantages for coating adherence, increased lubricating qualities, conversion to stable compounds, and cost-effectiveness. It lessens the amount of reactive chemicals on the metal surface, creates a shield against corrosive elements, promotes paint adhesion, and lessens wear on moving parts. It is a popular and cost-effective option due to its versatility, compatibility with various metals, and ability to cover complicated structures [5]. A variety of metals, including steel, iron, zinc-coated materials like galvanised steel, aluminum, and, to a lesser extent, copper, and brass can be phosphatized. Phosphatization is flexible and can be used on a wide range of metals. It increases friction, paint adherence, and corrosion resistance. The process formulation and parameters may change for different metals due to varying amounts of reactivity. When metal components need higher corrosion resistance and surface characteristics, such as in the automotive, aerospace, and equipment industries, phosphatization is frequently utilised [6]. By promoting rapid interaction between metal and phosphate ions, higher pH levels accelerate the formation of a phosphate coating during phosphating. The alkaline environment promotes the formation of stable metal phosphate compounds, which improves solubility and accelerates the deposition of the protective coating on the substrate. Low pH values, which cause acidic conditions, on the other hand, slow down the reaction rate and can result in less soluble or unstable molecules. Corrosion protection may be less effective due to delayed nucleation and growth of the phosphate layer. During the phosphating process, pH is critical in controlling the rate and quality of coating production.

This review paper explores the role of phosphatization in corrosion prevention, and explains the mechanisms involved. Various methods such as zinc phosphating, iron phosphating, and manganese phosphating are discussed and therefore highlight their specific applications and advantages. Additionally, we will delve into the factors influencing the phosphatization processes, such as solution composition, temperature, pH, and processing time. Furthermore, the paper will examine the characterization techniques used to analyse the quality and effectiveness of phosphatized coatings. This review paper will also discuss the ecological balance of phosphatization, offering eco-friendly substitutes to traditional corrosion prevention techniques. By critically analysing existing literature and research findings, this review paper seeks to consolidate the current knowledge on the phosphatization of metals for corrosion prevention. The comprehensive understanding of phosphatization processes, mechanisms, and applications will contribute to the development of more efficient and reliable corrosion protection strategies. Overall, the paper will serve as a valuable resource for researchers, engineers, and professionals interested in corrosion prevention.

Prologue of Phosphatization

Phosphatization, commonly referred to as phosphating, is a surface preparation technique that is frequently used in many industries to prepare metal surfaces for subsequent coating or painting treatments. In-depth knowledge of the phosphatization mechanisms and its protective benefits is the goal of this review work [7-9]. Starting with a thorough washing of the metal surface to get rid of impurities like oil, grease, rust, and scale, the procedure entails several crucial procedures [10, 11]. Before adding the phosphate coating, an activation solution is frequently employed as the initial stage in the phosphatization process. Use the activation solution to get the metal surface ready for the best adhesion and phosphate coating formation. Using this method, a stable and long-lasting phosphate layer must be created. The activation solution, which is often made up of acidic chemicals and surfactants, is used to remove surface contaminants, oxides, and oils from the metal surface to create a clear and receptive substrate for the subsequent phosphate coating.

The metal surface is submerged in a phosphating solution made up of metal phosphates, phosphoric acid, and additives. In this phase, chemical interactions on the metal surface result in the synthesis of metal phosphate compounds, which operate as a protective coating. Finally, a thorough rinse is carried out to get rid of any remaining chemicals and by products [12-15].

Phosphatization is carried out by several complex mechanisms. The solution's phosphoric acid displaces metal ions off the surface, which then interact with phosphate ions to form insoluble metal phosphate compounds that are then deposited on the metal surface. In addition to improving the adhesion of following coatings or paints, this conversion coating serves as a barrier against corrosion [16].

Phosphatization provides metal surfaces with protective qualities that are important. First, the process changes the metal surface into a more stable and corrosion-resistant state thanks to the conversion coating that is created. The metal phosphate layer serves as a barrier, keeping the metal away from corrosive substances including moisture, oxygen, and chemicals. The microscopic surface roughness that phosphatization produces also improves mechanical interlocking, promoting greater adhesion of following coatings or paints. As a result, the coating system will be stronger and longer lasting. In addition, the phosphatized surface has better lubricity and wear resistance, which lowers friction and lengthens the lifespan of treated components [17, 18].

Numerous industries, including the automotive, aerospace, building, and manufacturing ones, use phosphatization in diverse ways. It plays a key role in preparing metal surfaces for future coating applications or can be employed as a stand-alone corrosion protection technique. The phosphatization technique can be used by companies to improve corrosion resistance and encourage superior coating adhesion by comprehending its underlying mechanics and protective characteristics [19].

In conclusion, phosphatization is a flexible and effective surface modification technique that endows metal substrates with exceptional protective qualities. It is a valuable technology in industrial applications because it may produce a stable conversion coating and improve coating adherence. Industries may maximise the strength, firmness, stability, and durability of their metal components by using surface treatment like phosphatization [20].

Basic Phosphatization Process

Phosphatization process has certain process steps and sequences where three basic stages are there as pre-treatment, phosphatization layer deposition, and post-treatment [21]. Pre-treatment basically use to prepare the part for phosphatization coating layer deposition and post-treatment is liable to avoid any kind of post reaction after phosphatization coating layer deposited. The basic steps and sequences are as follows for the steel phosphatization process (Figure 1).

Degreasing

Degreasing step basically liable to remove the oil, grease, wax, dirt from the metal surface prior to phosphatzation for the strengthen deposition. In this process basically diluted alkaline chemicals such as sodium hydroxide, sodium bicarbonate, etc. with desired temperature up to 70 ˚C.

Water rinse

Water rinse is used basically to avoid carry over chemicals from the surface which will be deposited during degreasing process. In this process recommended demineralized water to optimize the quality of phosphatization.

De-rusting

De-rusting or pickling is basically liable to remove pre oxidation layer from the surface which may be occurs due to environmental aspect on bare metal surface. In this process widely being used diluted phosphoric acid and sulphuric acid with desired heating temperature up to 70 ˚C.

Water rinse

Water rinse is used basically to avoid carry over chemicals from the surface which will be deposited during de-rusting process. In this process recommended demineralized water having zero TDS to optimize the quality of phosphatization.

Activation

Activation process is basically being used to activate the surface for phosphatization process and to opt the coating thickness in uniform size and deposition. In this process basic chemical is titanium with basic nature chemicals. It works good at room temperature with pH nearly 9.5 to 10. Immersion time is between to 30 to 60 seconds to optimize a good uniform phosphate coating.

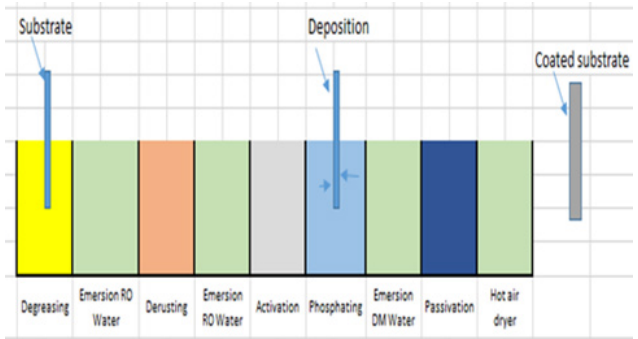

Figure 1: Steps and sequences for the steel phosphatizstion process.

Phosphatization of metal

Phosphatization is a kind of chemical treatment where we opt the thin coating layer of zinc, manganese, etc., this is the actual stage where we got the deposition of phosphate coating on the metal surface to improve the corrosion resistance and paint adhesion properties. The factors contribute to this process immersion bathe contains phosphate and phosphite anion in presence of suitable accelerators which may be nitrites. P ratio in phosphatization be as follows.

P ratio = phosphophyllite/phosphphyllite + hopeite

Phosphate coating can be measured by thickness, but it will not be uniform for all area due to its uneven crystal sizes. To measure the deposited coating weight on certain surface area is a good method to check the deposition of phosphate coating layer thickness.

Water rinse

Water rinse is used basically to avoid carry over chemicals from the surface which will be deposited during phosphating process. In this process recommended demineralized water having zero TDS to optimize the quality of phosphatization.

Passivation

Passivation is basically used to get the passivate of phosphate coated layers to protect form the other environment gaseous reaction which will be occurs after phosphatization and resulted hamper the quality of coating layer. In this process basically used diluted trivalent chrome chemical with a certain pH level and a certain temperature.

Dryer

After passivation it must be quick dry with hot air or natural air to avoid any other quality issues. For drying different dryers are used. Dryers may man-made hand dryers are electrical appliances.

Impact of Phosphatization on Different Metals

Below is the general image of steel metal after phosphatization. It looks dark grey (Figure 2). According to the chemistry laws every metal has different physical and chemical properties due to variations in their size-to-volume ratio, and number of valence electrons, thus, these metals act differently in the same reaction.

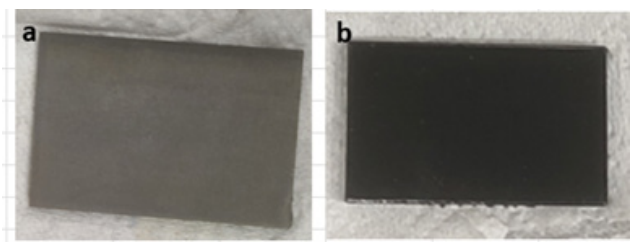

Figure 2: (**a**) Bare eye image of phosphatized part and (**b**) Pure polyester powder coated part.

Steel

It is one of the essential materials used in most industries due to its exceptional strength, durability, and versatility. Steel is an alloy consisting of iron and carbon with other manganese, chromium, nickel, and molybdenum to increase the efficacy. It has various applications thus protection of steel from corrosion has been a major task as it extends the lifespan of infrastructure and increases productivity. The exposure of steel to moisture, humidity, temperature, and agents like acid, base, and salts lead to the deterioration and degradation of the elements leading to corrosion. Thus, phosphatizing steel can prevent the material to corrode and improves paint adhesion. Iron phosphate coating on steel acts as a protective barrier against moisture, chemicals, and other corrosive agents, therefore increasing the lifespan of steel [22].

The phosphate coating, or iron coating offers surface preparation for other treatments like paint adhesion, lubrication, or cold forming process. It reduces friction, improves malleability, and enables better shaping without degradation the surface [23].

It also enhances the paint adhesion thus forming a rough and porous surface providing a better surface area and enhancing durability. These properties offered by steel after phosphatization are important for industries like automotive, construction, and manufacturing where steel components are exposed to harsh environments.

Aluminum

Aluminum is the most abundant metal found in earth's crust in its ore form called bauxite. It has a very low density and is lightweight and thus forms a protective oxide layer on its surface to prevent corrosion of the metal. It is enhanced when aluminum forms a protective layer of phosphates as it prevents direct contact of metal with corrosive agents, moisture, and temperature. The phosphate coating on aluminum enhances the paint adhesions, and lubrication as it reduces friction between many movable parts and promotes adhesion between the metal surface and adhesives. The visual appearance of coated material is also enhanced and is aesthetically attractive [24].

Zinc

Metals like zinc have all metallic properties like low melting point, softness and bluish white in color, and are extensively used in industries for galvanizing other metals as zinc layer on metals like steel or iron prevents their direct contact with moisture, temperature, etc. Like aluminum and steel, the phosphate layer on zinc metal enhances the corrosion resistance. It also improves painting adhesions, and lubrication. Phosphatization is a conversion process for zinc as it converts zinc into a protective layer [25].

Impact of Various Factors on Phosphate Coating

Change in composition

The phosphatization process includes phosphates coating and concentration of phosphoric acid in the chemical reaction and therefore its composition does affect the corrosion resistance. Different phosphate coatings like zinc coating, and manganese coating have different abilities to resist corrosion. The concentration of phosphoric acid and other components leads to variation in the thickness of the coating layer, thus higher concentration forms a thick layer having higher resistance than the lower concentration acid [26].

pH level

Chemical reactions during the phosphate coating are highly influenced by the pH level of the solution. The research has investigated that a higher pH level generally accelerates the formation of a coating on the substrate, while a lower pH level can slow down the deposition of phosphate coating. pH level needs to be maintained to get the desired product. It also influences the coating uniformity as it ensures the substrate has no patches and a continuous layer which in a result gives better adhesion. Therefore, pH level ensures substrate with good quality of coating and thus more corrosion resistance [27].

Temperature

Any chemical reaction is highly affected by the temperature as it increases the energy in the molecules leading to the collision of the particles and the formation of new molecules. Similarly, reaction during phosphatization is highly influenced by the temperature. Higher temperature hastens the reaction rate leading to faster coating formation. It also influences the thickness of the coating and therefore gives hardness and shows more resistance to corrosion. It can contribute to more resistant phosphate crystals [28].

Immersion time

Phosphate coating is directly proportional to the substrate's immersion time of the substrate into the phosphating solution. The longer the substrate is immersed more the thickness of the coating layer and thus more resistance towards corrosion. Like all other factors immersion time also influences the uniformity of the coating layer, density and size of the phosphate crystal and adhesion of the coating to the substrate. Therefore, control of these factors is important to get the desired product [29].

Metal surface and the phosphating solution

The interaction between the metal surface and the phosphate arrangement plays a key part in the arrangement of defensive layers to prevent corrosion. Phosphating could be a broadly utilized surface treatment strategy in which metal surfaces are inundated in an arrangement containing phosphoric acid and other debasements. The point of this inquiry is to discover out the chemical responses and components related to the interaction between the metal surface and the phosphate arrangement, which eventually leads to the arrangement of defensive layers. By understanding these forms, analysts can optimize phosphating strategies to make strides in erosion resistance and amplify the life of metal structures [30].

Metal surfaces are inclined to erosion, a dangerous

preparation that altogether influences the strength and auxiliary astuteness of different applications. Phosphating, moreover, known as phosphating or transformation coating, has developed as a viable strategy to anticipate erosion and move forward the attachment of hence-connected coatings. Amid phosphating, metal surfaces meet a phosphate arrangement, which ordinarily comprises of phosphoric corrosive, metal particles and different added substances such as quickening agents, inhibitors, and surfactants. Because of this preparation, a defensive layer shapes on the metal surface, which acts as an obstruction against destructive substances. Despite its broad utilization, the chemical responses and components included within the interaction between the metal surface and the phosphate arrangement are still complex and require advanced examination [31].

The interaction between the metal surface and the phosphate arrangement triggers an arrangement of chemical responses that lead to the arrangement of defensive layers. Phosphoric corrosive as the most component response with the metal surface, causing metal particles to break up and discharge hydrogen gas. The dissolved metal particles and the corrosive respond encourage to creation of metal phosphates, which accelerate and join to the metal surface. This phosphate layer acts as a corrosion-resistant obstruction, anticipating the spread of destructive substances and advancing the attachment of ensuing coatings. Added substances within the phosphate arrangement, such as quickening agents and surfactants, impact the response kinetics and the properties of the defensive layer shape [32].

The arrangement of defensive layers in phosphating could be a complex handle influenced by a few components, counting the composition of the phosphate arrangement, temperature, pH and metal surface properties. The morphology, thickness and composition of the defensive layer depends on the interaction between the metal surface and the arrangement. For case, the nearness of microstructures, oxides or debasements on the metal surface can affect the nucleation and development of the phosphate layer. In expansion, the concentration and sort of metal particles within the solution, as well as pH and temperature, can affect the arrangement of shapeless or crystalline phosphates and the ensuing attachment of the defensive layer [33].

To optimize phosphating processes and make strides in erosion resistance, it is vital to get the interaction between the metal surface and the phosphate arrangement. By illustrating the chemical responses and mechanisms included in the arrangement of defensive layers, analysts can move forward with the solidness and execution of metallic structures uncovered in cruel situations. Encourage inquiry about what is justified to examine the impact of diverse parameters on the phosphating handle and create moved-forward phosphating arrangements adjusted to metal substrates, progressing erosion security, and expanding benefit life [34].

Effectiveness of Different Phosphate Coating

Each metal has its own specific property depending on its atomic number, size, electronegativity, etc. Therefore, every metal reacts differently with phosphoric acid, and these results in different coating layers. Zinc phosphate crystals provide corrosion resistance to the iron-based substrates, which offer good adhesion and act as an excellent base for subsequent treatments like painting or powder coating. These coatings provide limited corrosion to the substrate thus this substrate has less chance of survival in highly corrosive environments. Iron phosphate forms an amorphous and crystalline layer on the steel-based substrate. They are distinctively used as pre-treatment for paints and adhesion as they provide less corrosion resistance than zinc and manganese. Whereas the manganese phosphate layer is believed to provide excellent corrosion resistance as they form a very dense manganese crystal layer. These are extensively used in very harsh marine environments [35].

The review paper investigates the most efficient phosphate coating for corrosion resistance. The ranking given to the coating according to the corrosion resistance is given below.

- Manganese phosphate
- Zinc phosphate
- Iron phosphate

Therefore, combining these phosphate coatings with other pre-treatment like paints, etc., can increase the efficacy of the desired product.

Characteristics of Phosphate Coating

Phosphate coatings have been found to altogether progress the attachment between the metal substrate and the connected defensive coating. The arrangement of the phosphate layer advances the nucleation of the defensive coating, which makes a solid bond between the surfaces. By expanding attachment, the probability of delamination or peeling of the coating is decreased, successfully securing the base metal against destructive substances. The phosphate coating acts as a middle-of-the-road layer, diminishing the hazard of galvanic erosion that regularly happens at the metal coating interface. In expansion, the moved forward attachment moves forward wear, which encourages securing the metal beneath extreme working conditions. The wettability of the metal surface may be an unequivocal figure affecting its erosion resistance. The hydrophobic surface repulses water and destructive fluids, diminishing the contact range and abating the corrosion process. Phosphate coatings can be planned to form metal surfaces hydrophobic utilizing different strategies, such as including hydrophobic specialists or altering the precious stone structure of the phosphate layer. The coming about diminish in dampness on the metal surface anticipates the arrangement and movement of erosion. In expansion, the hydrophobic nature of the phosphate-coated metal encourages self-cleaning properties, minimizing the collection of contaminants that can worsen erosion. Phosphate coatings lead to a controlled alteration within the microstructure of the metal, which makes strides in erosion resistance [36].

The coating handle starts with the arrangement of a fine-

grained homogeneous phosphate layer that impeccably covers the metal surface. This modified microstructure successfully acts as a boundary against forceful particles, anticipating them from coming to the metal surface and causing erosion. In expansion, the phosphate layer can act as a supply of erosion inhibitors, slowly discharging them over time to ensure the metal. In expansion, the enhancement of the microstructure diminishes the grain boundary engendering ways, which avoids the movement of neighbourhood erosion components. In rundown, phosphate coatings play a key part in adjusting different surface properties, counting attachment, wettability, and microstructure, to progress metal resistance to destructive situations. Phosphate coatings frame a solid defensive layer due to better attachment, which diminishes the probability of coating peeling and galvanic erosion. In expansion, the hydrophobicity of these coatings anticipates the maintenance of dampness and limits the improvement of erosion. In expansion, the adjusted microstructure acts as a boundary against destructive substances and encourages the expansion of erosion inhibitors. By understanding and utilizing the potential of phosphate coatings, the industry can successfully amplify the life and unwavering quality of metal parts uncovered in harsh and destructive situations [37-40].

Conclusion

The chemical reactions involved in the process is still not understood as the formation of phosphate layer is considered a complicated task. Obtaining desired product is a huge task as the proper concentration is taken. Phosphating processes involves hazardous chemicals leading to pollution and therefore eco-friendly alternatives that maintain high corrosion resistance is a significant task. Therefore, our researchers are working on bringing out best with process to maintain high corrosion resistance.

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Conflict of Interest

None.

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