DOI: https://doi.org/10.24425/amm.2023.145471

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PHOSPHATE CONVERSION COATING – A SHORT REVIEW

Phosphating is the process of depositing, by conversion, a layer of insoluble phosphate compounds, on the metal's surface. Although phosphate coatings have been studied since the early nineteenth century, they are not only still being studied, but are an area of interest due to their many applications. The advantages of these types of coatings are well known, such as the low cost of the deposition process, the improvement of corrosion resistance properties, and the improvement of wear resistance and adhesion of further deposited layers such as paint. All this, leads to studies on the constant improvement of the properties of the phosphate coating, by modifying the parameters of the phosphating process, as well as by modifying/replacing the substances used in the phosphating solutions with "environmentally friendly" solutions. Also due to these advantages, several researchers are studying the possibility of using phosphate coatings in fields such as civil engineering or medicine (biomaterials coatings). This paper aims to present some essential aspects of phosphating and to bring to the fore the latest research on "eco-friendly" phosphating solutions and the possibility of using the phosphating process in other fields, such as the medical field. Also, the paper aims to discuss the possibility of eliminating/reducing the harmful effect that the use of phosphating has on the environment.

Keywords: conversion coatings; phosphate; review; corrosion properties

1. Introduction

The metallic materials used in society are subjected to a continuous process of degradation of the structure, as a result of interactions with the environment, a process known as "corrosion" [1].

Except for noble metals, all other metals are unstable in contact with atmospheric air. How this instability manifests itself, as well as the degree to which it occurs, depends on both the nature of the metal and its vicinity. For example, in the case of ferrous materials, iron oxide is formed as a result of corrosion. This process of corrosion is called anti-metallurgy because it tends to bring the metals back to their natural state [2]. The natural state is represented by the combination of the elements of the metal with other elements, especially with oxygen, from which the metallic material is derived through the administration of energy [3]. Fig. 1 shows the process of steel manufacture and the appearance of iron oxides.

Metal corrosion mainly involves the energy sector, transport, chemicals, food, oil and mechanics [4,5]. The damage caused by this is enormous because it takes into account the intrinsic value of the corroded metal, the costs of replacing them and the costs of preventing the destructive process, in simple terms, these are called direct costs [6,7].

Indirect costs are those related to the reduction of the useful life of the metal, the loss of products, pollution, production

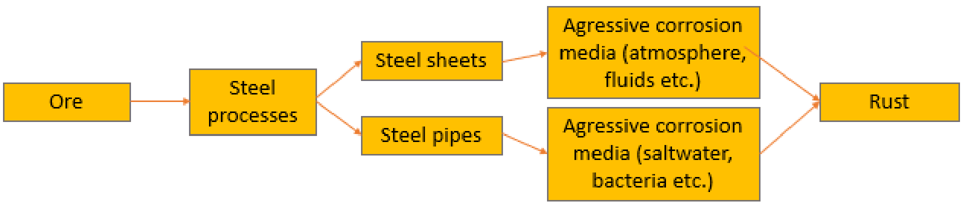

Fig. 1. The process of stell manufacture and appearance of oxides

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stoppage, sudden damage or explosion [8]. Indirect costs are difficult to predict and often exceed direct costs.

The costs associated with metal corrosion are very high. Corrosion generates high costs due to degradation of materials, by direct corrosion, but especially by decommissioning of objects and equipment made of metals [9,10]. Corrosion can also cause substantial repair costs to equipment components [11].

According to existing data, almost a third of the world's metal production is decommissioned due to corrosion. Since only about two-thirds of the corroded metal is recovered by smelting, it means that about 10% of world production is permanently lost as a result of the action of destroying corrosion [7,11,12].

These enormous damages demonstrate the need to systematically investigate the causes of corrosion and to develop effective means of combating it. The economic effects of corrosion protection are important. Thus, many studies show that the application of anti-corrosion protection means leads to great savings in the field of shipbuilding, civil engineering, chemical industry etc. [13-16].

Therefore, over time, multiple methods of metal protection against corrosion have been developed, including electrolytic depositions, spray coatings, diffusion coatings, cladding coatings, phosphating, oxidation, enamelling, painting, bituminous coatings, physical vapour deposition methods, and chemical vapour deposition methods [17-20].

Among these surface treatments, the chemical conversion treatment is a simple and cost-effective method, used in a wide range of applications, being one of the most practised methods of corrosion protection [21,22]. Phosphating is a method of corrosion protection that consists in converting the metal surface into a phosphate film by attacking with complex solutions containing phosphoric acid and oxides of zinc, manganese, iron, etc. [23]. Being a conversion layer, the phosphate film has very good adhesion to the support metal, achieving the adhesion of the entire protection system and through its absorbent and adsorbent properties, it improves the quality of the entire protection system [19,24,25]. Corrosion protection is due to the formation of a passivating layer, uniform and compact, consisting of a mixture of secondary and tertiary phosphates of zinc, manganese, calcium, etc., which are difficult to dissolve, obtained by coprecipitation or sequential precipitation in several stages, after prior pickling of iron-based metal surfaces [18,26-28].

Phosphating is a method of anticorrosive protection that consists in converting the metal surface into a phosphate film following chemical reactions formed between the phosphating solution and the substrate [25,27]. Depending on the formation conditions, the phosphate layer can have a crystalline or amorphous structure, the most used in anticorrosive protection being crystalline structures. Crystalline phosphating is a final or intermediate treatment that can be followed by mechanical operations and amorphous phosphating is a preliminary treatment for painting [29].

The first widespread use of phosphating took place in the United States in the manufacture of firearms during World War II. However, the earliest work on phosphating processes appeared in 1869-1906, and the first patent for iron phosphating was filed in the United States in 1907 by Thomas Watts Coslett. The first phosphating solution created was manganese-based, and in 1938 the patent for the zinc-based phosphating solution was obtained.

Over time, various patents have emerged regarding the change of phosphating solution, the introduction of new metal ions to improve the solution, reduce phosphating time, reduce the cost of the phosphating process, reduce the impact on the environment etc. [30-33]. However, the aim of this paper is to present some essential aspects of phosphating and to bring to the fore the latest research on „eco-friendly" phosphating solutions and the possibility of using the phosphating process in other fields, such as the medical field.

2. Phosphating process and phosphate solution composition

The stages of the phosphating process are different, their choice depending on the type and surface of the material on which the phosphate layer will be deposited and the chemical composition of the phosphating solutions used [22]. Fig. 2 shows the stages of the phosphating process, the most used solutions for cleaning/degreasing/pickling/activating the surface, some information about the phosphating process, but also SEM (scanning electron microscopy) and OM (optical microscopy) images with phosphate layers deposited with different phosphating solutions from the point view of the chemical composition.

Regardless of how the phosphating is performed, there are three main stages: preparation of the sample surface, phosphating and drying [34]. The surface preparation step has an important role in the characteristics of the phosphate layer obtained because if the surface is not completely cleaned and there are areas where are oxides or grease, the layer will be uneven. Also, at this stage, the surface of the metal will be activated in such a way that the layer deposited by the conversion is homogeneous [25].

Material surface preparation

Depending on the type and chemical composition of the material, the methods of surface preparation are different, but the only common step is to polish the surface of the metal with metallographic paper of different granules.

Regarding the surface preparation of the materials, this can be done by:

- ultrasonic cleaning – the parts are immersed in acetone or alcohol while the liquid is subjected to ultrasound [35];
- degreasing – the parts are immersed in solutions based on KOH [36], NaOH [36], Na_2CO_3[37] etc. in order to remove grease or oil particles, thus avoiding the partial activation or coating of the metal surface;
- pickling – the parts are immersed in solutions based on hydrochloric acid [35], clorhidric acid [28] and sulfuric

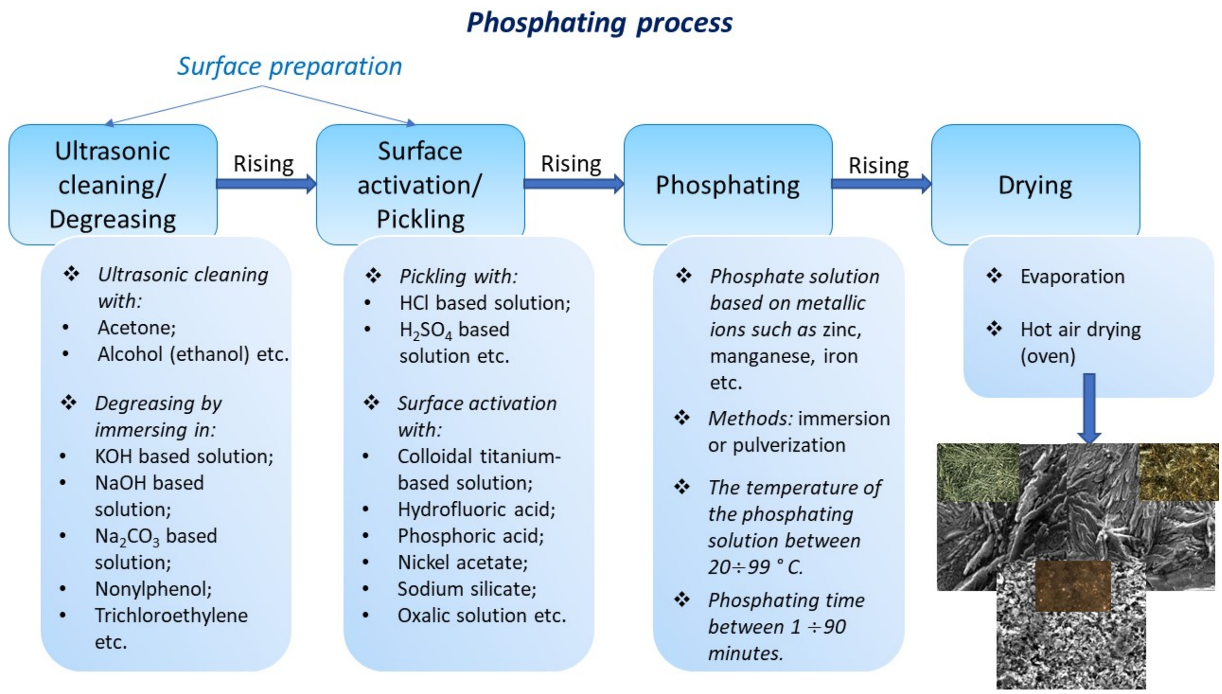

Fig. 2. The phosphating process

acid [22]. This is done in order to remove oxides formed on the surface of the metal and to activate the surface. Using acids in the pre-phosphating stage, uniformity of the surface and an improvement of the corrosion resistance properties of the phosphate layers obtained were observed [38];

- activation of the metal surface – the parts are immersed in solutions based on colloidal titanium [39], hydrofluoric acid [35], nickel acetate, sodium silicate [40], oxalic solution [41] etc. This stage aims to prepare the surface for nucleation and the growth of phosphate crystals.

Also, the cleaning of the sample surface can be done by mechanical methods, namely by sandblasting and brushing, but less used [22].

Phosphating

The deposition of the phosphate layer can be done by immersion or spraying, depending on the type of phosphating solution and the size and shape of the parts to be phosphate [29]. In terms of the deposition time of the phosphate layer, spraying is faster compared to immersion, but the layer deposited by immersion has better corrosion resistance and adhesion properties [26].

In immersion phosphating, the deposition time of the phosphate layer can be between 1 and 90 minutes, and the temperature of the phosphate bath can vary between 20 and 99°C, but to obtain an optimal coating speed and a quality of the layer. It is recommended that the bath temperature be between 30-60°C [34].

Regardless of the chemical composition of the phosphate solution, its acidity is an important factor in maintaining the equilibrium conditions of the phosphate bath, as the amount of free acid, total acid and the ratio between the two can influence the quality and uniformity of the phosphate layer [32].

To reduce the formation time of the phosphate layer, accelerators can be added to the phosphating solutions, such as nitric acid (HNO_3) [23], sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$), $NaNO_2$ [42] etc. In addition, to form a uniform and high-quality layer, activators such as sodium fluoride (NaF) [43], hydrogen fluoride (HF) [38] can be added to the phosphating solution.

Also in the phosphating solution can be added various additives that aim: to reduce the amount of sludge in the phosphating bath (citric acid, nitrobenzene sulphonate) [44], improve the properties of the deposited layer (nickel-metal ions (Ni), calcium (Ca), iron (Fe) etc.) [18], improving the chemical stability (sodium hydroxide (NaOH)) [34], to increase the duration of use of the solution (sodium tripolyphosphate ($Na_5P_3O_{10}$)) [22] etc.

Rumyantsev et al. [45] added a phosphating solution, used for cold phosphating, zinc nitrate and calcium nitrate, thus changing the colour of the phosphate layer to white. Analyzing the corrosion behaviour, it was observed that the white phosphate layer still has a low corrosion resistance compared to the conventional phosphate layer.

3. Properties of phosphate coatings

Compared to other deposition methods used, phosphating has the following advantages [22,35]:

- Low cost;
- Low impact on the mechanical properties of the substrate;
- High adhesion to the substrate (deposition by conversion);
- Simple deposition process;
- Excellent design and control capability;

- Provides better adhesion to subsequent layers (paint, oil);
- Introduction of the metallic elements → to promote bone formation, antibacterial and immunoregulatory;
- Obtaining morphological characteristics favourable to cell adhesion similar to related biological functions;
- Improving corrosion and wear resistance etc.

All these characteristics of phosphate layers are studied by multiple methods [35,36,46-51]:

- Structural, morphological and elemental points of view, using: scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Energy Dispersive X-Ray Analysis (EDX), X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) etc.;
- Corrosion behaviour is analysed using multiple methods such as drop method, potentiodynamic polarization (linear and cyclic polarization), salt spray test, electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), static immersion test etc. with different corrosive media: simulate body fluid (SBF), Hank's Balanced Salt Solution (HBSS), wastewater, seawater, fire extinguishing solution, rainwater etc.;
- Mechanical characteristics: Vickers hardness, adhesion test, scratch test, wear test etc.

Also, the surface characteristic of the layer as wettability, thickness and roughness is important. Therefore, the thickness of the layer can be measured using a coating thickness gauge and the roughness using Laser Scanning Confocal Microscopy (LSCM).

Regarding the deposition of phosphate layers on biomaterials, several analyzes are performed by different methods such as the immersion degradation test, in vitro osteoclast culture, hemocompatibility evaluation, cell morphology and adhesion, in vivo test etc.

4. The applications of phosphate coatings

Due to the many advantages of phosphate coatings, they are used in many fields, such as:

- In the automotive industry → cars, like other road vehicles, are exposed to aggressive agents that act on the body by corrosion, abrasion, erosion, etc. Aggressive attacks intensify in wet seasons, especially in winter when, due to salt and sand treatments on national roads, the aggressiveness of the environment increases. To increase the protection properties of organic films, special preoperative treatments for the preparation of metal surfaces are required [34];
- In civil engineering → to improve the corrosion resistance of reinforcing steel and the adhesion between steel and concrete [52];
- In the military industry → to improve the corrosion resistance of weapons [22];
- In the medical industry → improving the corrosion and wear resistance of biomaterials used in the manufacture of prostheses, also promotes osteointegration [35].
- In the plastic deformation processing industry → reduce the coefficient of friction, by improving the wear resistance and the adhesion to the lubricant [24].

5. Conclusions

The need to reduce costs by protecting metals against corrosion leads to the need for continuous study of coating methods. Therefore, taking into account the characteristics of the phosphate layers, as well as the low cost of the deposition process, it can be considered that phosphating is one of the most advantageous coating methods used to protect metals against corrosion.

The phosphating process, as well as the properties of the deposited layers, are intensively studied. Nevertheless, the impact of this solution on the environment is an important issue. Therefore, the researchers must find a solution to reduce this impact by adjusting the phosphating solution/phosphating process.

Acknowledgment

This paper was realized with the support of "Institutional development through increasing the innovation, development and research performance of TUIASI – COMPETE", project funded by contract no. 27PFE /2021, financed by the Romanian government. This paper was also supported by "Gheorghe Asachi" Technical University from Iaşi (TUIASI), through the Project "Performance and excellence in postdoctoral research 2022".

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