

Review Article

New Applications of Electroless Nickel-Phosphorus Composite Coatings in Various Industries: A Systematic Review**Sh. Mahboubizadeh^{1,*}, F. Badretaie², M. Mohammadi¹, S. Chizari², O. Ashkani¹**¹*Department of Materials Engineering, SR.C., Islamic Azad University, Tehran, Iran.*²*Department of Mechanical Engineering, NT.C., Islamic Azad University, Tehran, Iran.**Received: 05 July 2025 - Accepted: 08 December 2025***Abstract**

Metal coatings used in various industrial surfaces play an important role in the protection of industrial tools and parts, and the development of metal coating processes, together with reinforcing particles such as oxide, non-oxide ceramic particles, and nanostructure particles on the surfaces with different heterogeneous shapes, it has been welcomed by a large part of researchers. Such coatings can be produced by various methods, such as mechanical methods, electrochemical deposition, CVD, PVD, etc. Meanwhile, electroless nickel-phosphorus (ENP) composite coatings are important due to the possibility of coating asymmetric shapes and maintaining the uniformity of the composition, as well as the desired resistance to wear and corrosion. The use of these coatings has increased significantly in recent years, particularly in the manufacture of parts required by the automotive, aerospace, electrical, chemical, and oil and gas industries. In the forthcoming study, their nickel-phosphorus composite coatings have been investigated using the electroless method, and we will examine their mechanical and corrosion properties. It is noteworthy that nickel-phosphorus microdot arrays are also of interest today and could be a suitable field of research.

Keywords: Electroless Composite Coatings, NiP, Corrosion Resistance, Composite Coatings, Micro-dot Array.

1. Introduction

Corrosion is one of the fundamental problems of various industries, such as oil, gas, and power. In this regard, the construction and improvement of coatings that can protect the parts used in the oil, gas, and petrochemical industries has become an important issue, and the issue of equipment protection, transmission, and maintenance of energy such as oil and gas pipelines in tanks, valves, pipes and other equipment used in the mentioned industries against corrosion has led to the activity of many industrialists and researchers in the discussion of improving common coatings or making new coatings. To apply metal composite coatings, which is the subject of this article, electroless, electrochemical, and mechanical coating methods are often used. The electroless method has now been embraced and used by many researchers and industrialists because of the simplicity of the coating process, the simplicity of the production equipment, and the fact that no electricity is used. In addition to the advantages mentioned, electroless coatings have significant advantages in practical properties compared to electroplated coatings, which include hardness, high surface uniformity, corrosion resistance, electrical properties, and wear resistance [1]. Initially, in 1844, Wurtz [2] was able to deposit nickel on the surface of nickel metal by the electroless method and by reducing Ni^{2+} ions, but these coatings were not considered due to the unfavorable characteristics of the produced coating, such as roughness and weakness.

However, in 1946, Brenner and Riddel were able to obtain coatings with desirable properties by developing formulations and performing various tests, and since then, with the progress of tests and the study of various parameters affecting the material and process on the properties of this type of coating, the industrial use of electroless NiP coatings has been achieved [3].

Electroless NiP coatings include a large part of industrial metal coatings, which are often used with different amounts of phosphorus, which increases the amount of phosphorus in this category of coatings, leading to increased corrosion resistance and increased wear resistance, and In general, their metallurgical properties depend on the amount of phosphorus in it [4].

In this regard, NiP coatings are divided into three categories:

- Low phosphorus, phosphorus content 1-7 wt.% .
- Medium phosphorus, phosphorus content 7-10 Wt%.
- High phosphorus, the amount of phosphorus 10-12 Wt% .

In the following article, an attempt has been made to study and examine the conditions of manufacturing electroless nickel-phosphorus composite coatings and to study their properties due to the addition of different particles to the coating, which with the expansion of the use of these coatings, various industrial needs for these coatings have increased. has found in the following, the composition of the required electrolyte bath will be examined.

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2. Bath composition for electroless nickel-phosphorus coatings

The idea of producing electroless Ni P (phosphorus nickel) composite coatings is to deposit the secondary phase of solid particles in electroless nickel (phosphorus) coatings and benefit from their uniformity, hardness, corrosion resistance and wear resistance. The effectiveness of precipitation depends on the chemistry of the bath, the nature of the particles and the operating conditions. The most important part of electroless plating is the creation of an electroless bath and the addition of various factors that affect it.

2.1. Source of Ni^{2+} ions

For example, nickel sulphate or nickel chloride, the nickel ion accepts electrons from the reducing agent, which is the electron donor, and the bottom surface becomes nickel metal [5, 6].

2.2. Reducing Agent

Known as a source of electrons for the reduction of metal ions. Sodium hypophosphite monohydrate is mainly used as a reducing agent to provide active hydrogen atoms for catalytic dehydrogenation to reduce nickel ions to metal and provide the phosphorus part of the deposited alloy [7].

2.3. Complexing Agents

Complexing factors include organic acids or their salts (maleic, succinic or citric acid), which are added to control the reactions and prevent the decomposition of the solution, i.e. they prevent the formation of an excess concentration of free metal ions. The plating rate is inversely related to the stability of the ion complex. They also act as buffers (neutral) and inhibitors of nickel phosphite precipitation. The complexing factors used have a significant effect on sediment quality and internal stress and porosity levels [8, 9].

2.4. Stabilizers or Accelerators

Used in small quantities and in the ppm range, it is often added to increase the sedimentation rate and to weaken the bond between the hydrogen and phosphorus atoms in the hypophosphite molecules in order to facilitate the absorption of phosphorus on the catalyst surface, including lead, Pb, cadmium and Cd ions. Molybdenum, Mo, arsenic, As, tin, Sn, thorium, Th, and malic acid are mentioned as stabilizers, and succinic acid is also used as an accelerator [10, 11].

2.5. Temperature

It acts as the energy driver for deposition and is considered to be an important variable of the electroless electrolyte bath, so temperature should be

controlled as it affects the kinetics and rate of deposition for high quality coatings. Electroless NiP deposition occurs at temperatures of 60 degrees Celsius and above, and the deposition rate increases exponentially with temperature.[11,12] A low temperature leads to a decrease in energy and reduces the amount of deposition, whereas a very high temperature activates the electrolyte bath and leads to bath instability.

2.6. PH Regulator

pH is an important parameter because it affects the amount of phosphorus in the sediment, i.e. a higher pH value reduces the amount of phosphorus in the sediment and vice versa, which can be adjusted using sodium hydroxide or sulphuric acid [13]. Based on this, two types of Electroless NiP baths can be formed.

Alkaline and acidic NiP Electroless baths with the following characteristics: Acidic NiP baths have more favorable properties than alkaline baths and have higher compositional stability. When acid baths are used, it is easier to control the percentage of phosphorus in the sediment, which is the main factor controlling the sediment properties, and they have higher thermal stability, so the use of acid baths is prioritized in various industries, especially in corrosion applications [14, 15].

2.7. Effects of Heat Treatment

It is one of the factors influencing the structure and properties of the coating. For example, electroless nickel-phosphorus coatings undergo different structural changes under the influence of different temperatures [16,17].

And this has obvious effects on wear resistance, conductivity and non-conductivity resistance and friction properties. Based on the crystallization process formed in electroless nickel-phosphorus coatings, two types of structures can be observed:

i. Alloy coating containing nickel with a microcrystalline structure as the main composition in the deposited state.

ii. alloy coating with an amorphous phase which does not contain the microcrystalline nickel structure as a major component.

If there is a coating containing 10.8% phosphorus in which the dominant nickel structure is microcrystalline, it should be annealed at low temperatures of 200 to 300 degrees Celsius for 4 hours. The result of this process is the formation of microcrystalline nickel phases Ni_{12}P_5 and Ni_3P at all temperatures and often leads to an increase in hardness due to the formation of nickel phosphide Ni_3P [18], but this amount decreases at temperatures above 400 degrees Celsius due to the formation of defects. network and coarsening of the Ni_3P particles [19, 20].

Generally, crystalline nickel and Ni₃P phases are observed during annealing and at temperatures above 400-600 degrees Celsius [21].

The studies by Zhao et al [22] investigated the effect of low temperature annealing on the properties of amorphous NiP alloy coatings over different time periods. It was found that the micro hardness decreased initially and then increased with time. In another study, Nava et al [23] investigated the effect of heat treatment at temperatures higher than 500 to 600 degrees Celsius on the corrosion resistance of nickel-phosphorus coatings containing 10.6% phosphorus. It was found that the corrosion resistance decreased as the annealing temperature increased. In conclusion, the values in Table. 1. can be used to construct a good electroless plating bath.

Table. 1. Optimized condition of Electroless NiP composites.

Compound used	Content	Ref.
Nickel Sulfate	25-35 g/L	[24]
Sodium hypophosphite	35-45 g/L	
Lactic acid	32-38 mL/L	
Stabilizer	1 ppm	
PH	6	

3. NiP Electroless composite coatings

In recent years, a lot of attention has been paid to the production of their composite coatings, which have shown better properties and characteristics than the usual NiP coatings. By incorporating Al₂O₃, into the NiP metal matrix, favorable composite coatings have been achieved in such a way that the functional particles are uniformly and completely distributed in the electroless nickel matrix, which is firmly bonded to the matrix layer. In theory, almost any type of particle can be co-deposited as long as it can withstand the conditions in the electroless nickel bath and is of the right size. In the following, in addition to examining the research of researchers in the field of nanocomposite coatings and the ways to enhance their various properties, which ultimately increases the applications of such coatings in various industries and in environments with corrosive and abrasive atmospheres. In this regard, the advantages of electroless composite plating over conventional composite plating techniques include deposit quality, uniformity and excellent tribological properties [25], leading to an increase in the production of electroless composite coatings such as a wide range of composite coatings. Phosphorous nickel is electroless. Fig. 1. shows the different particles used in electroless nickel-phosphorus composite coatings [26-42].

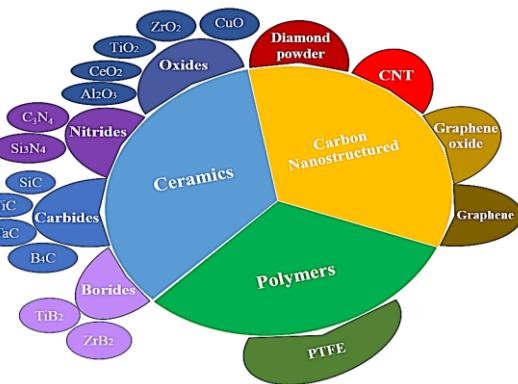


Fig. 1. Investigation of some types of reinforcing particles of electroless nickel-phosphorus composite coatings.

Initially, the use of composite electroless scrubbers was unsuccessful and often resulted in the failure of the electroless bath due to the dispersion of fine particles that increased the surface area of the electroless bath to approximately 700-800 bar. However, the problem was solved by the use of suitable stabilizers. Research into the use of second phase particles in electroless nickel baths began in the early 1960s. Later, Odekerken et al [43] succeeded in producing the primary coating by using an interlayer of finely dispersed particles within the metal matrix. In the period 1970-1980, research on electroless composite coatings was in its infancy. Since then, there are almost 200 articles in the Scopus database, the oldest of which is entitled "Recent advances in electroless nickel deposition" [44].

Next, in 1976, Metzger et al [45] developed electroless nickel coatings containing micron-sized alumina (Al₂O₃) particles. A few years later, the first commercial application of SiC Electroless composite coatings was for the Wankel internal combustion engine, and another commercial composite was coded as nickel-phosphorus-polytetrafluoroethylene (NiP-PTFE) in 1981 [46].

However, the simultaneous deposition of diamond and PTFE particles was more challenging than the synthesis of composites containing Al₂O₃ or SiC. In the following years and with the introduction of nanotechnology, the possibility of combining sub-micron to Nano-sized reinforcing particles in a new generation metal/alloy matrix introduced composite coatings [47].

In electroless nickel-phosphorus composite coatings, the reinforcing particles are uniformly and completely distributed in the electroless nickel matrix, which is firmly bonded to the matrix layer. Theoretically, almost any type of particle can be co-deposited as long as it can withstand the conditions in the electroless nickel bath and is of the correct size. The proposed electroless composite coatings include a nickel phosphorus metal base with hard reinforcing particles such as silicon carbide, diamond, aluminum

oxide and tungsten, and it is often accompanied by the addition of these particles into the NiP electrolytic bath [48, 49].

Sometimes, instead of using hard and strong reinforcing particles, particles with lubricating properties are used, among which fluoropolymers, molybdenum disulphide and graphite can be mentioned [46] that the participation of reinforcing particles The coating is related to the growth of the surrounding deposits and there is no molecular bond between the NiP (nickel-phosphorus) matrix and the precipitated particles. The concentration of reinforcing particles in the plating bath affects the continuity of the surface. The simultaneous deposition of matrix and reinforcement improves the properties of these coatings, including wear resistance, lubricity and oxidation resistance.

In general, strong composite coatings require high adhesion between the reinforcing particles and the NiP Electroless bath matrix. Some important conditions for improving the quality of NiP Electroless composite coatings are particle size, mixing and stirring and electrolyte bathing stability. Surfactants are usually used to uniformly distribute the hard particles in the nickel-phosphorus (NiP) matrix and can be classified as anionic, cationic or non-ionic surfactants. Initially, the preparation of NiP Electroless composite coatings was not successful because the addition of fine reinforcing particles increased the instability of the bath [50]. To solve this problem, researchers decided to add suitable stabilizers such as thiourea and malic acid to the electroless bath, which resulted in preventing the rotation of reinforcing particles in the suspension bath and eventually their sedimentation, thus solving the problem of bath stability and the preparation of the composite coating. Fig. 2. shows the necessary criteria for the correct distribution of the rein forcers in the Electroless bath [51].

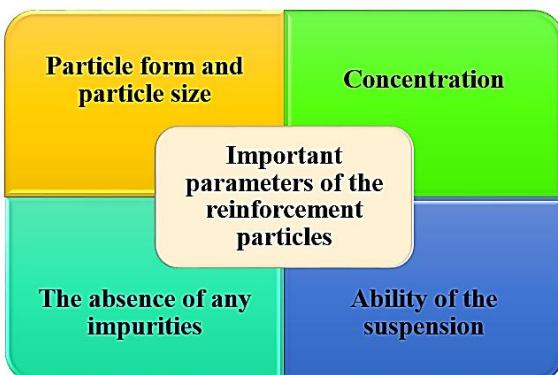


Fig. 2. Important parameters for the reinforcement particles of electroless composite coatings.

In another study, the effect of adding titanium to ANP coatings was investigated. The results showed that with increasing the amount of titanium particles, the

formed surface becomes uneven, and if the particle size reaches a critical limit, a phenomenon called spatial occlusion occurs, which affects the entry of particles onto the coating surfaces, which can cause changes in the coating. Considering this, it is suggested that researchers investigate the spatial occlusion phenomenon in coatings in other coating methods [52, 53]. Also, Ghavidel and his colleagues [54] investigated the effect of adding SiC to the Electroless NiP plating bath. In this experiment, it was found that adding 1 g/L of SiC nanoparticles with a size of 40 to 60 nm reduces corrosion resistance, but increasing this amount to 2 g/L worsens corrosion properties. It is noteworthy that samples containing 1 g/L of SiC had a uniform surface without any holes, indicating strong adhesion and corrosion protection. However, in samples containing 2 g/L SiC, the structure is uneven and the particles are concentrated in certain areas, which leads to porosity and can reduce the surface properties and corrosion resistance. The addition of various additives can also be an important topic and discussed in future research by researchers.

4. Investigation of the properties of electroless nickel-phosphorus composite coatings

In general terms, the properties of the proposed coatings can be considered as follows, each of which will be examined below.

4.1. Corrosion Resistance

The properties of nickel-phosphorus coatings depend mainly on the phosphorus content, which determines the structure of the coating. Accordingly, the microstructure of ENP coatings can be amorphous, crystalline or both. However, in addition to the amount of phosphorus, many factors affect the degree of crystallinity, such as the heating rate, heat treatment temperature and heat treatment time [39]. However, in general, the higher the amount of P in the ENP coating and the gamma amorphous structure, the higher the corrosion resistance [30, 55-57].

4.1.1. Adherence to Surfaces

Higher surface adhesion means greater protection of the substrate from corrosion. Meanwhile, electroless nickel-phosphorus coatings produce relatively strong and desirable adhesion due to the formation of metal bonds with the substrate. For example, Sundaraj et al [58] investigated the effect of the surfactant N-dodecyl betaine on electroless nickel-phosphorus composite coatings containing zinc oxide nanoparticles. Cracking and delamination were observed.

4.2. Wear Resistance

Many factors affect the final surface of electrolessly prepared samples, including: particle composition in terms of hardness and softness, wetting agents, surface treatments, inhibitors, etc. The surface roughness is one of the basic parameters to determine the wear resistance of the deposit because it is in direct contact with the metal surface during the process, which in turn provides better resistance to friction [59]. The addition of particles to the NiP coating changes the composition of the deposit. Therefore, the roughness and morphology are also affected. As the amount of phosphorus in the deposit increases, the roughness decreases and a brighter appearance is produced [60]. As the surface roughness of the coating increases, wear resistance is improved. In the table 2, some of the surface and wear properties of nickel-phosphorus composite coatings containing oxide particles have been investigated.

4.3. Micro-Hardness

Micro-hardness is considered as one of the mechanical properties of coatings and the addition of SiC-TiO₂-Al₂O₃ nanoparticles to electroless nickel phosphorus coatings increases the micro-hardness, for example, nickel phosphorus coatings containing TiO₂ nanoparticles after heat treatment at 400 degrees Celsius show the maximum micro-hardness of 1124 HV [61].

4.4. Surface Morphology

The addition of nanoparticles changes the morphology of the nickel-phosphorus coatings and leads to a more uniform distribution of the particles in the matrix, this uniformity is necessary to achieve stable mechanical and electrochemical properties throughout the coating surface [5]. Table. 2. Investigation of the effect of particles in nickel-phosphorus electroless composite coatings [11]. Much research has concluded that the heat treatment process can change the structure of the coatings produced from amorphous to crystalline. Surface roughness is an undesirable property in coatings because it causes friction and wear. However, in a lubricated environment, it helps to retain the oil and prevent welding. In general, the electroless process produces a very good surface because it follows the surface for deposition rather than filling the gaps between particles [15].

The amount of surface porosity indicates the quality of the coating produced and the level of corrosion resistance and adhesion of the coating to the substrate. If the resulting coating has open holes, the possibility of severe galvanic corrosion is increased. In this type of corrosion, the holes act as anodes and other coating surfaces act as cathodes, increasing the rate of corrosion and destroying the coating. Factors

that affect the amount of porosity include roughness, surface morphology and coating thickness. One of the factors that reduces the porosity of the coating is heat treatment. This reduces the rate of corrosion of coated surfaces.

Table. 2. Investigation of the properties of electroless nickel-phase composite coatings.

Particle type	Particles	Hardness	Corrosion Resistance
Oxides	Al ₂ O ₃	Improved with heat treated coatings	Improved
	TiO ₂	Increased	Improved
	ZrO ₂	Increased	Improved
	SiO ₂	Increased	Ineffective
Carbides	SiC		Ineffective
Carbon Nano structured	CNT	Increased but decreased when limit content is reached	Ineffective
Polymer	PTFE	Decreased	Ineffective

4. Applications

Electroless nickel-phosphorus composite coatings have been widely used in various industries due to their favorable mechanical and chemical properties such as corrosion resistance and wear resistance, which can be used in automotive industry and parts. They are used in the oil and gas industry to protect pistons and crankshafts from corrosion and wear by reducing friction, to improve the performance and life of automotive parts, and in the electronics industry to make parts that do not stop [53]. Fig. 3. shows an important part of the applications for this category of coatings.

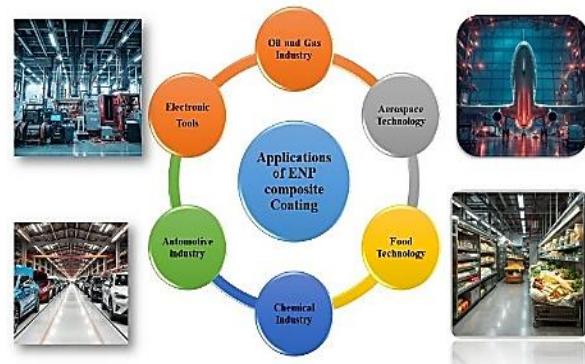


Fig. 3. Investigation of different applications of electroless nickel-phosphorus composite coatings.

5.1. Nano and Quantum technology and ENP Coating

Finally, one of the important points is the development of ENP coatings in combination with

Nano-materials and quantum dots. Quantum dots can play a key role in the development of electronic components due to various properties such as high conductivity. There are limited results in this field and research indicates the use of carbon nanotubes [62]. In this field, it is necessary for researchers to take important steps and it is suggested that quantum dots be added as an additive to ANP coating compositions and its properties should be discussed and investigated.

6. Conclusion

As shown in this systematic review, the general aspects of ENP coatings are very widely used and important. In this study, various aspects, main mechanisms and some requirements of this process were investigated and finally, the results showed that these compounds can be effective for controlling and reducing corrosion.

It is worth mentioning that in the future, it is suggested that researchers focus their research on other developments such as multiple composites. The use of composite materials such as zirconium oxide, titanium oxide and nickel is suggested and also their combination with aluminum oxide and selenium oxide may be able to increase corrosion resistance, which is a desirable research area.

In addition to the points mentioned, it is suggested that the use of nanoparticles and quantum dots in coatings be put on the agenda. The demand for quality coatings and environmental protection can lead to the use of Nano methods and the use of quantum dots because these materials generally lead to the enhancement of the properties of the base material and may also lead to long-term environmental protection. Increasing efficiency is one of the reasons that can lead to environmental protection, and the use of quantum dots in coatings can provide a basis for appropriate research.

Declarations statements

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflicts of interest

The authors declare that there is no conflict of interest.

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