



## Surface Coatings on Steel Pipes Used in Oil and Gas Industries - A Review

Muhammad Mumtaz Mirza<sup>1\*</sup>, Elansezhian Rasu<sup>1</sup> and Anjali Desilva<sup>2</sup>

<sup>1</sup>Department of Mechanical and Industrial Engineering, Caledonian College of Engineering, Seeb, CPO 111, Sultanate of Oman.

<sup>2</sup>School of Engineering and Built Environment, Glasgow Caledonian University, Glasgow, Scotland, UK.

### Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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### ABSTRACT

This paper discusses the characteristics and classifications of different type of protective coatings being used in oil and gas industry. After a brief review of the fundamental aspects of organic and powder coatings, this paper discusses the investigation being done on the tribological and mechanical properties of electroless Ni-P (EN-P) composite coatings. The study covers its fundamental aspects, mechanical properties, applications and future trends. EN-P coating have found wide applications in aerospace, automobile, electrical and chemical industries but in the field of oil and gas pipelines, very little research has been done. Since EN-P coatings possess splendid tribological properties, technological advancement demands further improvement in newer variants of EN-P coatings like Ni-W-P, Ni-Cu-P, Ni-P-SiC, Ni-P-TiO<sub>2</sub> and so on to find the optimum coating solutions in the field of oil and gas pipelines and its variants against corrosion.

**Keywords:** Corrosion; electroless composite coatings; oil and gas; tribological properties.

\*Corresponding author: E-mail: [mumtazyousafi2000@gmail.com](mailto:mumtazyousafi2000@gmail.com);

## 1. INTRODUCTION

Pipelines play an important role throughout the world as a means of transporting gases and liquids over long distances from their source to the supply. Generally three types of pipelines are used in the world with, a) gathering lines for shorter distance and with diameter size up to 4 inches, b) feeder lines connecting from oil storage to transmission lines bigger in size as compared to gathering lines c) with transmission lines (maximum 48 inches in diameter) are the main form of oil supply [1]. Pipelines exposed to the atmosphere alleviate problem of generating corrosion on its surface. According to U.S. Department of Transportation data between 1994 and 1999, approximately 25% of all reported accidents were due to corrosion of which 65% were due to external corrosion and 35% were due to internal corrosion [2].

Corrosion is the oxidation of a metal due to an electrochemical reaction. The oxidizing agent is most often  $O_2$  (atmospheric corrosion) or  $H^+$  (chemical corrosion) or both. Generally oil and gas pipelines are made of low alloy steel ASTM A106 B [3]. These materials are primarily composed of iron (98 to 99 percent iron), small amount of carbon (0.001 to 0.30 percent by weight), manganese (0.30 to 1.50 percent by weight) and other intentionally added alloying elements in small amounts (niobium, molybdenum, vanadium, titanium) [4]. The extraction of base metals from their ores requires a significant amount of energy. Since these metals are thermodynamically stable in their pure form, they will tend to oxidize to a lower energy state, and such process is commonly termed as corrosion [5].

To protect the pipeline from corrosion, the very first attempt is to isolate the pipeline surface from contact with the surrounding, so that no corrosion could occur. This concept is entirely reasonable and logical. Furthermore, a coating would be effective, if the coating material is an electrical insulator. To make the coating more effective in performance, most operators plan coatings in combination with Cathodic Protection (CP) that provides necessary protection on most of the pipeline surface on which it is applied.

## 2. COATING CHARACTERISTICS

Some typical coatings characteristics for oil and gas pipelines are [6]:

### 2.1 Effective Electrical Insulator

Corrosion is an electrochemical process and a coating has to block the current flow by isolating the pipe from its installed environment/electrolyte, therefore the coating should have a strong dielectric strength.

### 2.2 Effective Moisture Barrier

Low level of water absorption is desirable, it increases the effectiveness of CP.

### 2.3 Applicability

Application of the coating to the pipe must be possible by a method that will not have any adverse effects on the properties of the pipe.

### 2.4 Good Adhesion to Pipe Surface

Good adhesion and cohesion are vital parameters for anticorrosive coatings.

### 2.5 Ability to Withstand Normal Handling / Installation

The coating must protect against damage as a function of its impact, abrasion and flexibility characteristics.

### 2.6 Resistance to Disbanding

Most pipelines are CP, it is directly proportional to the quality and reliability of the coating.

### 2.7 Ease of Repair

Field repairs / field-coating should be carried out easily.

### 2.8 Nontoxic Interaction with the Environment

Selection must confirm to the modification, restriction or banned due to the environmental / health standards.

## 3. COATING SELECTION CRITERIA

In addition to the above properties, the following generic factors may be considered when selecting a pipeline coating [6]:-

- Type of environment
- Accessibility of pipeline

Ambient temperature during applications  
 Operating temperature of pipeline  
 Type of coating  
 Cost including overheads  
 Pipe surface preparation requirements

provides limited resistance to sulfur, amines, oxygen and other oxidants.

#### 4. COATING CLASSIFICATIONS

Coatings can be classified into two main categories as per their resistance to corrosion, namely organic and inorganic coatings. Below is a brief description of each [7]:-

**Organic Coatings** Epoxy, polyurethane, chlorinated rubber and polyvinyl chloride coatings act as a barrier to corrosion.

**Inorganic Coatings** includes coatings such as ceramics and glass.

#### 5.2 Fusion Bonded Epoxy (FBE)

*Advantages:* Chemical resistance, improved thermal dimensional stability and minimal hysteresis.

*Disadvantages:* The material is expensive and the pipe and its coating must be heated to 250°F. This requires highly skilled labour.

#### 5.3 Coal Tar Enamel (CTE)

*Advantages:* Very low cost.

*Disadvantages:* Gives minimal protection and is highly toxic and flammable.

#### 5. CURRENT TRENDS IN COATINGS

Currently there are four well known methods for coating pipelines [8]:

##### 5.1 Three-Layer PE (3LPE)/PP (3LPP)

*Advantages:* Relatively low material and application cost

*Disadvantages:* Requires flame application to cause adhesion, that is dangerous in environment of a pipeline. It offers limited heat resistance of maximum 225°F – 250°F and lacks dimensional stability and borderline hardness. It

#### 5.4 Asphalt Enamel and Polyurethane (PUR)

*Advantages:* It is inexpensive and much better than Coal Tar Enamel. It reduces the hysteresis and its field repair is easy.

*Disadvantages:* It has poor resistance to chemicals and high ambient temperature. It lacks any dimensional stability.

#### 6. COATING TYPE AND MARKET SHARE

Typical market trends for different type of coatings [9] are shown in Fig. 1.

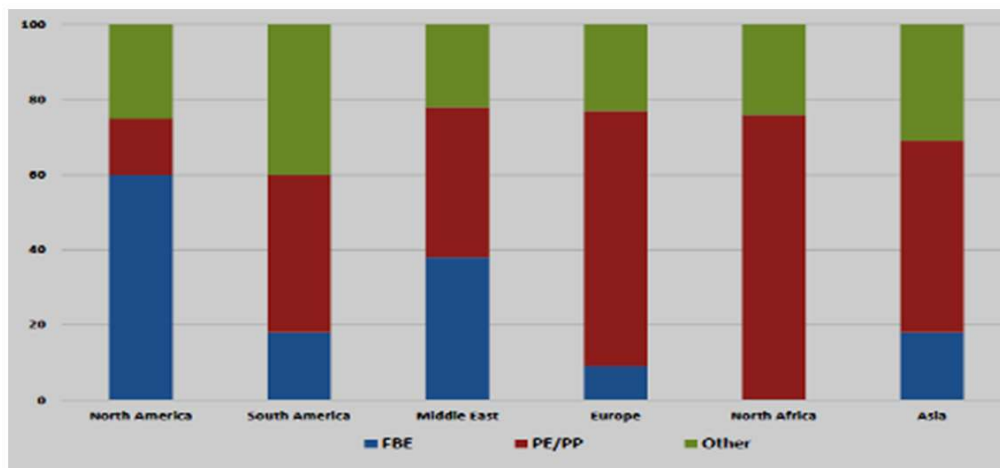
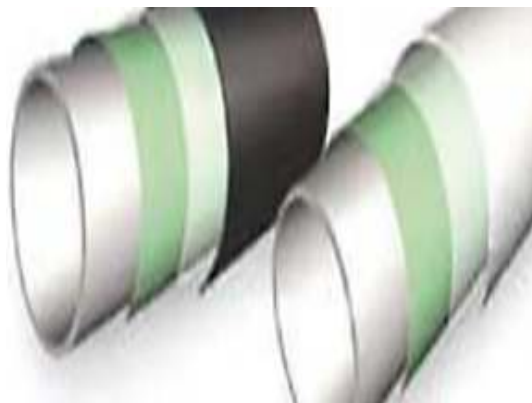


Fig. 1. Market trends [9]

## 7. OVERVIEW ON EXTERNAL COATINGS

Pipe line coatings could be internal or external. The coatings designed for external pipeline applications must be prepared in a way that it withstands different environmental conditions. Factors such as soil stress, soil born chemicals and salt water presence will affect the performance of external coatings [10].

Fusion-bonded epoxy (FBE) and a three-layer polyolefin (3LPO) (polyethylene or polypropylene) are presently the most popular external anti-corrosion coating systems in use. Fig. 2 represent the structure of 3LPO and FBE coatings [11]. Single-layer FBE is most popular in North America, Saudi Arabia, and the UK whereas the dual-layer FBE is favorite in Australia. The 3LPO coatings dominate the rest of the world's coating markets [12].



Coating Cross-Section	Material	Standard Thickness
		microns (mils)
	Polyethylene topcoat	500 (20)
	FBE/Adhesive Interlayer	125 ( 5)
	FBE	125 ( 5)
	<b>TOTAL</b>	<b>750 (30)</b>
	<b>STEEL</b>	

**Fig. 2. 3LPO coating and FBE coatings [11,12]**

Over the last few decades, (EN-P) electroless nickel phosphorous based protective coatings have played an important role against corrosion. It is basically an autocatalytic electrochemical oxidation and reduction process. The oxidation of a substance is recognized by loss of electrons

with reduction involves addition of electrons. Because of its simple construction and lack of involvement of electricity, it is one of the preferred coating processes in most of the industries [13]. The utilization of its novel properties include enhanced micro-hardness, good surface finish, great imperviousness to wear and corrosion resistance. The EN-P coatings are widely used in chemical, aerospace, automobile and electronic industries [14].

## 8. LITERATURE REVIEW ON EXTERNAL COATINGS

Extensive literature review of interest has been done on protective coatings for oil pipelines against external surface corrosion. This includes for various kinds of coatings in general and electroless coatings in particular. In the electroless coatings, the matrix is either Ni-P or Ni-B, depending on the nature of reducing agents used in the bath. This manuscript summarizes the properties based on Ni and Ni-P alloys and their composites. Furthermore, the review is divided into two main groups; (a) short review on organic / powder coatings and (b) EN-P coatings.

### 8.1 Short Review on Organic / Powder Coatings

#### 8.1.1 Historical overview

Wetting is an important factor that affects the ability of a coating to be intact with the metal to gauge its overall performance. Protective coatings are designed to offer high electrical resistance between the cathode and anode of the corrosion cell. Pipe surface becomes cathode and the anode is usually separated only by micrometers. The success of breaking the electrical conductivity between these electrodes depends on the ability of the coating to place itself between them. To achieve this, the coatings should have low viscosity. This is particularly important for coatings applied over a blast cleaned surface with deep profiles (between 2.5 and 4.5 mil).

Fusion bonded epoxy (FBE) was introduced in Europe in 1953 for the coating of electrical equipment by the liquid bed dipping method [15]. In the early 1960s it was introduced to the pipeline industry for the protection of small diameter water and oil field production piping. The first FBE for large diameter pipe was supplied in the mid-60s. By the late 70s, FBE became the most widely used pipeline coating in

the U.S., Canada, Saudi Arabia and the U.K. Presently, FBE is used in every continent for the protection of pipelines, production tubing and drill pipelines. It has also gained acceptance for the protection of reinforcing steel (rebar) in the U.S., Canada, U.K. and the Middle East [16].

Although FBE is an extremely successful corrosion protection system for underground pipelines, there are some inherent limitations that make the achievement of total corrosion protection difficult with coatings alone. These limitations are due to the chemical nature of organic material and the coating application procedure. To overcome the deficiency and achieve total corrosion protection, an alternative method of Cathodic Protection (CP) was used in combination with the coating. Presently, FBE with the CP system is the most effective and economical corrosion control system for underground pipelines, but the success depends on the coating's ability to become an integral part of the "CP coating" combination system itself.

Samimi studied the corrosion in pipeline coatings which is one of the main problems in oil and gas industries causing a large amount of money to be spent each year. The durability and permanence of adhesiveness depends on coating properties including its resistance to moisture penetration for three polyethylene layers [17]. Another research indicates that the long term anti-corrosion protection of buried pipelines is linked to the good barrier properties of the coating which needs to have good adhesion to withstand severe conditions of temperature and humidity [18]. To overcome the limitations, many researchers attempted to provide various solutions to the rising problems. Pratt and discussed the development of an FBE coating that could either be a standalone coating or a primer in a multi-layer system [19]. A research paper investigation on the role of Polyurethane as the thermoset polymer on various applications has been carried out which discusses the analysis on coating specifications of gas and oil transitional pipelines and compared their properties and common qualities. The author reported that the new FBE could be applied at temperatures as low as 180°C [20].

Amadi et al. [21] examined the anti-corrosion coating as an alternative to cementitious materials besides organic polymeric materials that have long been considered for pipe coatings. This is due to their good corrosion resistance, imperviousness to water and air, resistance to salinity, immunity to large variations in pH and

chemical and physical stabilities at moderately high temperatures. In the research, different types of anti-corrosion coatings were evaluated to consider their performance following different type of test [21]. Another paper is a continuation of this research work in which a new surface tolerant FBE pipe coating was developed. This coating tolerated a wide steel surface temperature window of 200 to 240°C. In this paper, the development of a new range of FBE coatings based on this new technology for pipe, valve, and rebar was discussed. Six Sigma tools were also used extensively in developing the program [22].

Aguirre studies the accelerated aging at high temperature coupled with extrapolation that employed to predict the service life of FBE coatings. This approach assumes that the aging mechanism at high temperatures is the same as it is at the actual service temperature of the coating, which is unlikely to be the case. This could prove to be a more valid method to predict service life of FBE coatings [23].

Guan in 2010 evaluated the increased demand for new oil and gas pipelines over the years for more innovative pipeline coating technologies. It intimates three key drivers behind the increased demand for new oil and gas pipelines: a) about 1.8 percent yearly growth in world energy demand; b) about 6.7 percent yearly depletion in world energy production; and c) technological developments associated with new reserves in more challenging locations [24].

Oki in 2015 presents current knowledge on corrosion and the monitoring of internal and external corrosion phenomena in the transmission and distribution of the pipelines in petroleum industry. The conjoint use of in-line inspection techniques (ILI) and side stream monitoring techniques were highly favored in order to eliminate catastrophic failures as a result of internal pipeline corrosion problems. External corrosion phenomena in pipelines were adequately monitored through the deployment of electrode potential measurements using suitable reference electrodes. Improvements in pipeline coatings applications were highlighted and the often neglected chromating procedure prior to coating application was addressed [25].

New advancements in FBE coating technology have led to the availability of dramatically improved coating materials and systems to address specific pipeline construction needs to

enable the coating to function under a wide variety of corrosive conditions. A review of FBE pipe coatings was presented, progressing from their early years to the next-generation materials. FBE coating solutions for the corrosion mitigation of pipeline systems ranging from its use as a stand-alone external coating to the foundation layer of a three-layer coating were included [26].

Kehr et al. [27] investigate about the pipelines that operate at high temperature requiring new coating material protection. Development of these coating materials requires new chemistry and testing methods. This paper reviewed coating requirements and existing test procedures applicable to high temperature. It proposed new testing methods for better evaluation of the new coatings that included test data and results.

One of the authors examined the polymer coating systems that is classically applied on a metal surface to provide a dense barrier against the corrosive species. In addition to coatings, CP is used for many applications to protect the metal structures from corrosive attack when the coating is damaged. However, the current demand would increase with the disbonded areas. Moreover, the reactions that take place at the cathode can cause a progressive enlargement of the unbounded area. Self-healing coatings are considered as an alternative route for efficient anticorrosion protection while maintaining a low demand in CP. Such coatings typically incorporate micro or nano capsules that contain film-formers and repair the coating damage when the coating is scratched. The paper describes the principle of this novel self-healing concept and discusses the healing efficiency on the basis of laboratory results [28].

Investigation on nanotechnology was also analyzed for manufacturing, analysis and use of structures for layers or tubes of less than 100 nanometers (nm) in at least one dimension. This

paper reviews different kinds of coatings, different types of pigments used in paint formulation and a special focus is set on the use of nano materials/fillers in coating application. More emphasis was given to bestow an insight in nano composite coating [29].

## 8.2 Review of EN-P Coatings

### 8.2.1 Historical overview

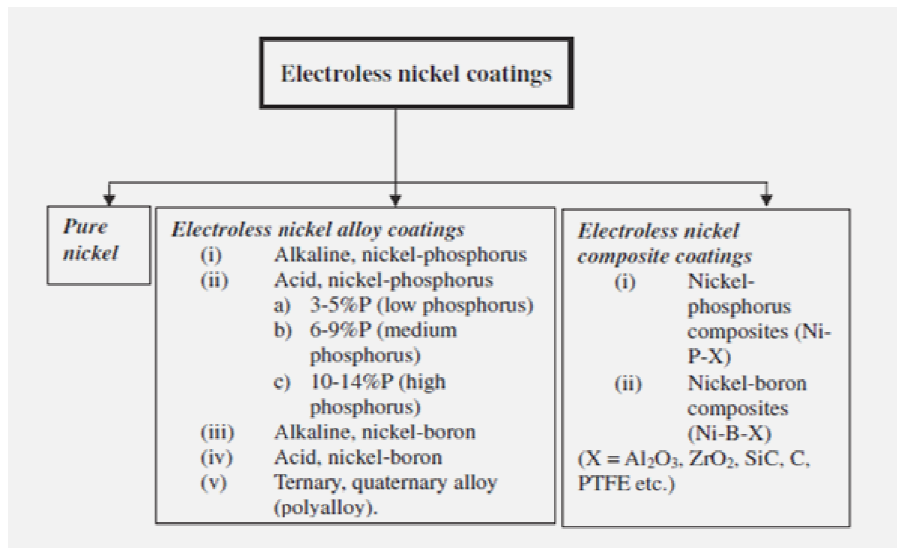
In 1844, Wurtz found out that the metallic nickel could be deposited from an aqueous solution of its salt by reduction with hypophosphite [30]. But the metal which was formed was in powder form. Later, researchers Breteau [31] and Roux [32] took bright coatings on all surfaces in a reaction vessel when the reducing agent had been added. However, these baths decomposed spontaneously and formed deposits on any surface that interacted with the solution, even on the walls of the container. Other investigators analysed the process but their interest revolved around the chemical reaction instead of the plating process. The discovery of electroless nickel technology as it is used today was developed in 1946 by Brenner et al. [33]. Brenner was the first to refer the process as 'Electroless'. These coatings can be divided into three main categories which are alloy, composite and metallic coatings.

EN-P coatings have been used either as protective or decorative coatings in industries such as electronics, computer, aerospace, printing, automotive, textile, plastics, optics and paper, food [34]. Some of the outstanding characteristics of EN-P coatings are superior corrosion and wear resistance, excellent uniformity, wide range of thickness, good solder ability and improved mechanical and physical properties [35]. General categories of EN coatings are shown in Fig. 3.

The components of EN bath and their composition are shown in Table 1 below [36].

**Table 1. EN bath composition and their function [36]**

Components	Functions
Nickel Ion source of metal	Reducing agent source of electrons
Complexants stabilizes the solution	Accelerators activates reducing agent
Buffers controlling pH (long term)	pH regulators
Nickel Ion source of metal	Reducing agent Source of electrons
Complexants stabilizes the solution	Accelerators activates reducing agent
Buffers controlling pH (long term)	pH regulators
Stabilizer Prevents solution breakdown	Wetting agents Increases wettability of the surfaces
Stabilizer Prevents solution breakdown	Wetting agents Increases wettability of the surfaces



**Fig. 3. General categories of EN [35]**

Over the years, the researchers have focused on its properties and applications that have been investigated further and expanded by many researchers to its present state of development.

### **8.2.2 Present status**

The current review is mostly focused on improving the tribological as well as mechanical properties of the EN-P coatings that covers fundamental aspects (nickel recovery efficiency, addition of reducing agents, changing EN bath composition and techniques through surfactants, heat treatment and special treatments) and mechanical properties. Moreover, future trends in EN-P coating will also be discussed in the end.

### **8.2.3 Fundamental aspects**

#### *8.2.3.1 Nickel Recovery Efficiency (NRE)*

The EN recovery efficiency is considered to be poor in the order of only 25% as reported in literature [37]. Some of the nickel particles formed during coating deposits on the substrate surface while the rest of them escape from the substrate, which is not useful and hence it is a waste [38,39]. An attempt is made to enhance the nickel recovery efficiency (NRE) by adding the concept of passive additives such as surfactants, stabilizers, accelerator and excess reducing agent. The impact of adding passive additives to the electroless bath are the areas which were not explored adequately by the previous researchers. NRE was not significantly

impacted by the addition of surfactants such as Sodium Dodecyl Sulfate (SDS) and Cetyl Trimethyl Ammonium Bromide (CTAB). However the coating efficiency is enhanced by 95% [40].

Elansezhan et al. [40,41] reported on the enhancement of NRE and micro hardness of the EN-P coating process by using Taguchi optimization technique (TOT). Currently, in the EN coating process, the NRE is very low. Because of this, the coating cost of EN is very high. Earlier researchers have attempted to recover the nickel from the used bath after coating is completed and some achieved success in their attempt by further improving the nickel recovery from 25 to 35%. To overcome the above issue, the excess volume of reducing agent (RA) is supplied to the bath during the coating process to compensate for the consumed amount of electrons. The impact of adding 50% of RA [41] on NRE and other properties of the deposit has been researched. The NRE significantly increased from 35 to 61%. The different coatings parameters put to use in the electroless bath were optimized to get the high NRE through TOT [42].

#### *8.2.3.2 Addition of Reducing Agent (RA)*

The objective of a RA is to supply electrons for the reduction of nickel. Different RA has been used in electroless coating of alloys. The four type of RA to be utilized for electroless nickel bath including Sodium hypophosphite, amineboranes, sodium borohydride, and hydrazine as shown in Table 2 below [43].

**Table 2. Reducing agent for EN plating [43]**

Deposit	Reducing Agent	Remarks
Ni-P	Sodium hypophosphite ( $\text{NaH}_2\text{PO}_2$ )	Acid or alkaline bath (2–17% P)
Ni-B	Sodium borohydride ( $\text{NaBH}_4$ ) Aminoborane (DMAB)	Hydrazine ( $\text{NH}_2\text{NH}_2$ ) Alkaline bath (0.5–10% B)
Only Ni	Hydrazine ( $\text{NH}_2\text{NH}_2$ )	Alkaline bath

Sodium hypophosphite (SHP) baths: More than 70% EN is deposited from the solutions reduced by sodium hypophosphite. The main plus points of these solutions over those reduced by borohydride or hydrazine includes lower costs and better ease of process control etc.

Kumar, [14] reported to retrieve more nickel ions from the bath, the amount of reducing agent i.e. SHP needed during the reaction was predicted and added in the bath to enhance the efficiency. The impact of adding excess volume of reducing agent on the coating efficiency, surface structure, phosphorous content in the deposit, wear, adhesion and corrosion behavior was examined. The results reported that the coating efficiency was enhanced to 30% while the wear resistance of the deposit was improved to 34% when compared to the substrate produced without excess RA. The coating efficiency without excess RA was reported to be only 62.5%. With the constant addition of the predicted amount of RA, all the Ni ions were transformed into Ni particles and coated over the substrate; thereby improving the coating efficiency to 90%.

### 8.2.3.3 Complexing agents

Complexing agents (chelates) are supposed to control the free nickel available to the reaction. There are three principal functions that complexing agents execute in the EN plating bath [44] a) they exert a buffering action that prevents the pH of the solution from falling too quickly b) they lessen the precipitation of nickel salts, e.g., basic salts or phosphites c) they lessen the concentration of free nickel ions by creating meta-stable complexes. Moreover, the complexing agent also impacts the reaction mechanism and deposition rate and hence the deposit. Usually all complexing agents follow an inverted bell shaped curve when their concentration is compared with the deposition rate i.e. there is a specific concentration when the deposition rate is maximum. The deposition rate slowly increases up to that optimum concentration and then drops. In case of reduction by hypophosphite, the ideal concentration for sodium citrate which acts as

the complexing agent is about 30 gpl [45]. Ethylene demine is the famously used complexing agent in case of reduction by borohydride. The ideal concentration for ethylene demine is reported to be 90 gpl [46]. Ammonium fluoride enhances the deposition rate and the buffering capability of Ni-P bath [47].

One of the complications of reduction reactions or chemical plating is the maintenance of the bath composition. As the plating continues, continuous lessening of the rate of reduction of nickel happens. The solutions cannot be replenished because of the formation of nickel phosphite. If nickel phosphite is precipitated in the bath, the surface quality of coating deteriorates leading to rough and dark coatings. Moreover, the nickel concentration in the solution also gets reduced and the bath goes to the verge of total decomposition. Sodium citrate decreases the formation of nickel phosphite and lessens the rate of deposition [48]. The ability to form nickel complexes is due to some of the proposed additives like salts of glycolic, succinic or malonic acids. However, these fail to block the precipitation of nickel phosphite. The best readings are obtained when the sodium citrate concentration is about 30 gpl. It helps in checking the coating from becoming porous and dull. Due to the reduction in rate of deposition, accelerators like salts of carbonic acids, soluble fluorides and inhibitors like thiourea can also be added to prevent the total decomposition of the bath. Bi, Pb, Cd and Te additions act as bath stabilizers [49]. Bismuth and Te seem to be less efficient than Pb and Cd in bath stabilization. These stabilizers are added in concentrations of just a few parts per million.

### 8.2.3.4 Effect of surfactants

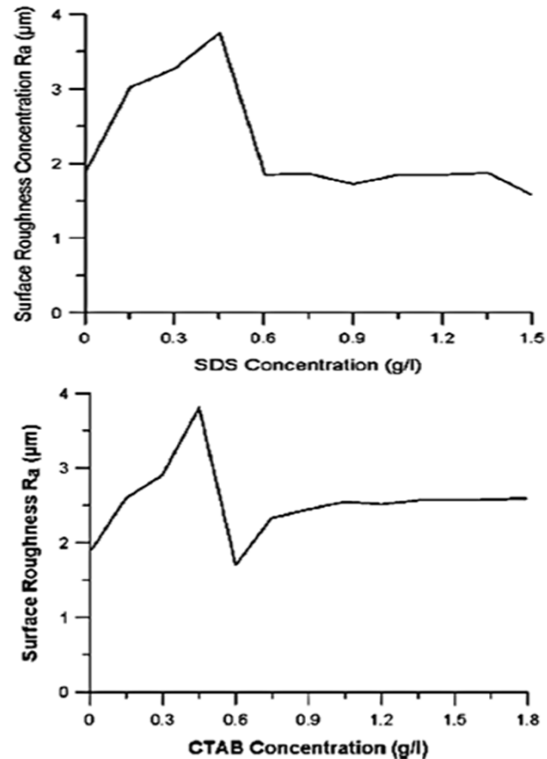
Surfactants are wetting agents that lessen the surface tension of a liquid, leading to easier spreading, and lower the interfacial tension between two liquids or a liquid and solid surface. In an EN bath, presence of surfactant encourages the coating deposition reaction between the bath solution and the immersed substrate surface.



Elansezhian et al. [40,50,51] studied the impact of two surfactants viz. Sodium dodecylsulfate (SDS) and Cetyltrimethyl ammonium bromide (CTAB) on the surface topography and amorphous phase of EN-P coating. It was discovered that surface finish of the coated layer significantly enhanced when the concentration of the surfactant exceeded about 0.6 gpl and the crystallite size was reported to vary from 20 nm with no surfactant to 8 nm with addition of surfactants. But at the lower levels of concentration the surface finish was reported to be poor [52]. Kesavan et al. [40] examine the effect of SDS and CTAB on the surface roughness, surface morphology and surface topography of EN-P surface protective coating taken from an alkaline bath. In this study the impact of surfactant concentrations on the surface roughness of coated samples were put under investigation. It was seen that the surface roughness, surface morphology and surface topography of Ni-P coating were clearly impacted by the addition of surfactants SDS and CTAB. EN deposits with addition of surfactant SDS and CTAB at a concentration of 0.6 gpl produces a smooth surface and the average roughness (Ra) value is 1.715  $\mu\text{m}$  for SDS and 1.607  $\mu\text{m}$  for CTAB which is less than the Ra value of EN deposit without surfactant addition of 1.885  $\mu\text{m}$ . The mean average roughness (Ra) value with addition of surfactant is 1.796  $\mu\text{m}$ . EN deposit with addition of surfactants contains a significant fraction of particles of nickel. In the presence of SDS, fine nickel particles have dispersed uniformly on the substrate surface leading to smoother surface finish of the deposited layers. In the presence of CTAB, at lower concentrations up to 0.6 gpl nickel particles have been deposited on the substrate surface and at the greater concentration above 0.6 gpl uniformly enhanced the surface finish of the deposited layer is resulted as shown in Fig. 4 [40].

Jiang [53] confers about Magnesium and how its alloys corrode rapidly in the electrolyte bath. Surfactants while used extensively as surface active agents in the electrolyte bath, have been little studied on magnesium surfaces. The impact of surfactants CTAB and SLS on the surface properties such as roughness, morphology and topography of EN-P deposits on magnesium alloy was examined. The researcher reported that the surfactant solution has significant impact on the composition of coating, surface roughness and surface morphology. In addition, it has marginal impact on the micro hardness.

Electroless coatings with addition of surfactants creates a smooth surface and average roughness value of 1.412  $\mu\text{m}$  for CTAB and 1.789  $\mu\text{m}$  for SLS, which are less than the value of 2.98  $\mu\text{m}$  without surfactant addition.



**Fig. 4. Average surface roughness of EN deposits vs. concentration (a) SDS, (b) CTAB [40]**

Elansezhian [54] researches about optimizing EN-P coating on the magnesium component with the addition of Nano-additives of ZnO, Al<sub>2</sub>O<sub>3</sub> and SiO as surfactants. Parameters studied such as surface roughness, micro-hardness, specific wear rate and surface morphology. The result revealed by addition of nano additives with surfactant affects the surface morphology that transformed the surface to a smooth surface. It explains the volume of nickel deposited, enhanced the substrate surface which lead to better wet-ability of nickel- phosphorous.

Another researcher worked on [55] impact of Zwitterionic surfactant consisting of positive and negative charges on its head is introduced in electroless alkaline bath to lessen the cost of electroless plating in industrial applications. The concentration of surfactant varied from 0 to 0.030 gpl instead of 0.006 gpl. The surfactant exhibits

attractive and repulsive forces in the electrolyte used, and their corresponding impact on coating thickness, surface structure, adhesion, specific wear rate and micro-hardness was examined. The results reported that there was an enhancement in the properties of coated substrate. Without Zwitterionic surfactant, the coating thickness was 44.31  $\mu\text{m}$ , and with surfactant at 0.018 gpl, it was increased to 98.03  $\mu\text{m}$ . The wear resistance of coated substrate was enhanced to 54% when compared with the substrate coated without surfactant. Without addition of surfactant, the micro-hardness was 432 HV, and with Zwitterionic surfactant at critical micelle concentration, it was increased to 680 HV.

Aamir [56] examined Ck45 Steel that was EN-P alloy from a bath containing SHP and different complexing agents (sodium citrate, sodium acetate and lactic acid). The impact of different complexing agents on phosphorus content, morphology, structure and hardness of the deposits was investigated. The anti-corrosion properties of Ni-P coatings were examined in 3.5% NaCl solution by the weight loss and potentiodynamic polarization technique being adopted. It has been reported that Ni-P coating obtained using sodium citrate complexing agent with the spherical nodular structure and smooth surface showed greater micro hardness and resistance to anti-corrosion. Mumtaz et al. had investigated about EN-P coatings with nano additives of CuO [125] and  $\text{Al}_2\text{O}_3$  [126] separately. He identified a novel method in which EN-P coatings with nano additives of CuO and

$\text{Al}_2\text{O}_3$  gives high corrosion resistance when examined on the external surface of oil pipelines used in Oman oil industry.

### 8.2.3.5 Effect of heat treatment

Heat-treatment is a vital factor that impacts on the thickness, hardness, structure and morphology of deposit [57]. When EN films of different phosphorous contents are heat treated at different temperatures, the phases present in the as-deposited films undergo definite structural changes. The crystallization behavior of EN-P can be categorized as follows a) alloy consisting microcrystalline nickel as a major constituent in the as deposited state and b) alloy only consists amorphous phase which do not have microcrystalline nickel as major constituent. It is reported to lessen the corrosion resistance of electroless coatings invariably. This is due to the change of microstructure of the coatings when heat treated [58]. Typical micro-hardness of some commercially available EN with different alloys with and without heat treated is presented in Figs. 5 and 6 below [43,36].

The alloy containing 10.8% P consists of microcrystalline structure as major constituent. When this alloy is annealed at a lower temperature range of 200 to 300°C for 4 hrs,  $\text{Ni}_{12}\text{P}_5$  microcrystalline nickel and  $\text{Ni}_3\text{P}$  are seen as common phases at all temperatures. While annealing at higher temperature of 400 to 600°C the usually observed phases are crystalline nickel and  $\text{Ni}_3\text{P}$  this shows these components can be obtained after complete

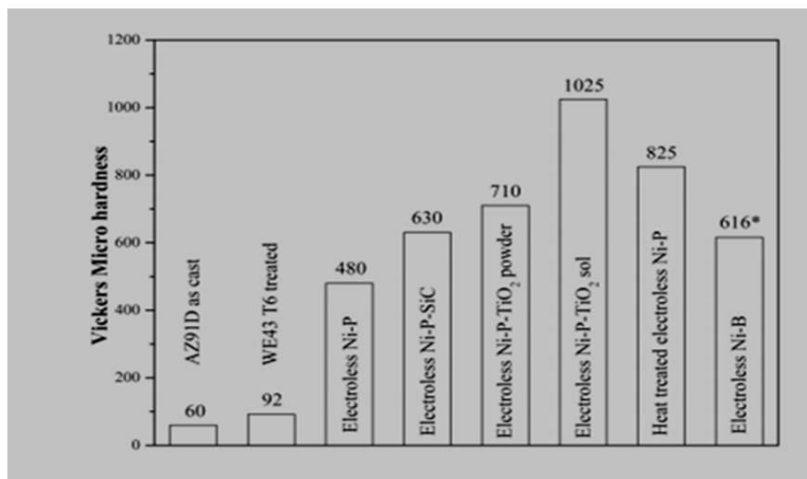
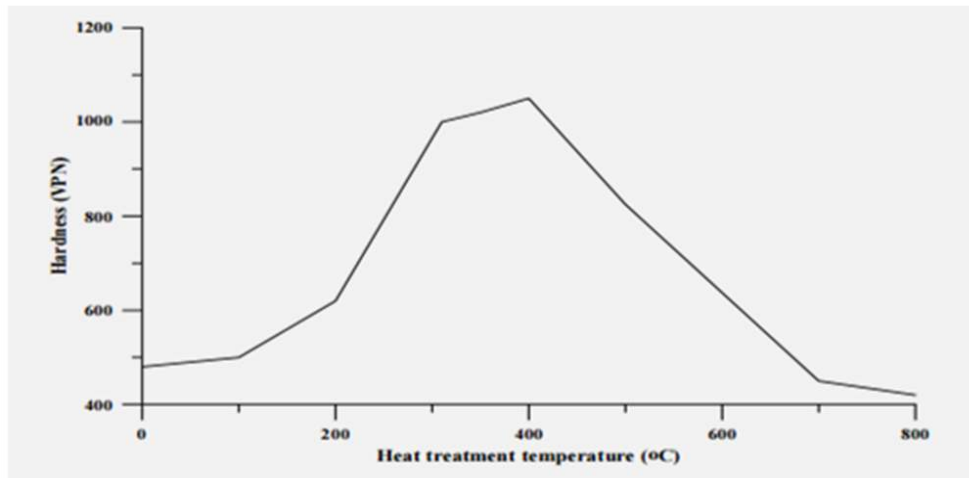


Fig. 5. Micro-hardness of EN coatings [59 to 64]



**Fig. 6. Effect of heat treatment on the hardness of EN-P [59 to 64]**

crystallization [65,66]. The only transition phase in this case is  $Ni_{12}P_5$  except no transition precipitates during annealing ED microcrystalline N-P films. The formation of the transition phase  $Ni_{12}P_5$  may be considered as the common property transition precipitate created while heating electroless microcrystalline nickel in the range of 200 to 300°C [67].

Leon [68] used pin on disc test that performed on Ni-P coatings, as deposited and heat treated at 200, 300, and 400°C for 1 hour, to examine the impact of heat treatment on the friction coefficient and wear resistance of the coatings. Heat treatment at 400°C induces complete crystallization of the ductile Ni-P matrix to  $Ni_3P$  and Ni, which is responsible for the highest hardness and wear resistance. Scanning electron micrographs of the wear tracks of the coating demonstrates that adhesive and abrasive wear are the wear mechanisms involved in the wear of Ni-P autocatalytic coatings under the dry non-lubricated conditions.

Srinivasan in his paper examines that electroless coatings in as-deposited condition usually exhibit an amorphous structure which imparts higher corrosion resistance. But, heat treatment induces crystallinity into the deposits, which leads to increase the grain boundaries that form active sites for corrosion attack [69]. To improve the hardness and the abrasion resistance of En-P deposits, heat treatments are performed. Studies carried out in this direction showed that a maximum hardness can be obtained after a heat treatment at 400°C for 1 h, when the hardness of the deposit improved from 500–600 up to 1000–

1100  $HV_{100}$  [70]. Michal Novak [71] describes evolution of tribological properties of En-P based coatings during heat treatment. Coatings were prepared using nickel lactate- hypophosphite bath with conventional  $AlSi_{10}Mg_3$  cast alloy used as a substrate. Coated samples were then heat treated at 400 – 550°C for 1 – 8 hours using pin on disk test. It was discovered that intermetallic phases formed during heat treatment because of the diffusion of nickel into the substrate greatly decrease wear resistance of coatings.

Nava work [72] reports the results obtained from a study of the effects of thermal treatment on the tribological characteristics (hardness, wear resistance, and coefficient of friction) and corrosion resistance of electrodeposited Ni-P coatings (10.6 at.% P). The XRD results demonstrate that the Ni-P alloy containing 10.6 at.% phosphorus was amorphous in nature. An improved hardness and lowered wear coefficient were observed after heat treatment for 60 min at 500°C because of the formation of a  $Ni_3P$  phase.

Jin [73] studied electroless nickel plating with potassium titanate whisker were co-deposited on medium carbon steel substrates. The microstructure of the composite coatings was studied. The impact of aging temperature on the microstructure of the composite coatings was examined using X-ray diffraction. The results demonstrated that the composite coatings will turn into crystal state with increasing heat treatment temperature after heat treatment at 400°C for 1 hour. The corrosion resistance and tribological properties of the composite coatings are not any less than those of EN-P coating.

## 8.2.4 Special treatments

### 8.2.4.1 The effect of hydrogen

The impact of charging and out gassing on friction and wear of Ni–P amorphous and nano crystalline coating has been examined by Zhou et al. [74]. It is observed that atomic hydrogen enriching on the surface lubricates the surface in contact, causing reduction in the friction coefficient and enhancement the wear durability. The wear durability is seen to be reversible as it can be restored after out gassing.

### 8.2.4.2 Laser treatment

Garsia [75] undertakes an investigation about how the corrosion behavior is usually determined by the presence of cracks in the coatings. It is demonstrated that the initial corrosion rates of the EN-P coatings submitted to laser treatment are lesser than those in EN-P coatings without laser treatment. Lu [76] investigates corrosion behaviors of the coatings before and after laser treatments were analysed by anodic polarization in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and immersion test in 10% weight HCl solution. The results indicated that the laser treatment produced nano crystalline Ni phase and Ni<sub>3</sub>P precipitation with remaining amorphous structure. Corrosion performance of the coatings was greatly improved by the laser treatment. Similarly another investigator [77] used laser as indicated in his paper of a comparative study of nano crystallization and the wear resistance of EN-P/Ni-W-P duplex coatings with a single Ni-W-P coating before and after high- power diode laser treatment. The findings revealed that in the case of laser treatment, the Ni-P/Ni-W-P duplex coatings offered better wear resistance than the single Ni-W-P coating, while the as-plated, single Ni-W-P coating showed better wear resistance than the Ni-P/Ni-W-P duplex coatings. Gordani et al. [78] have applied laser surface applying (LSA) to achieve a good metallurgical bonding between aluminum alloy substrate and Ni–P coating. The impact of alloying depth as a function of power density of laser is shown in Fig. 7. Both surface hardness and corrosion resistance is seen to increase by this process. Moreover, the best hardness and corrosion resistance is seen to develop at a laser scanning rate of 37 mm/min [79].

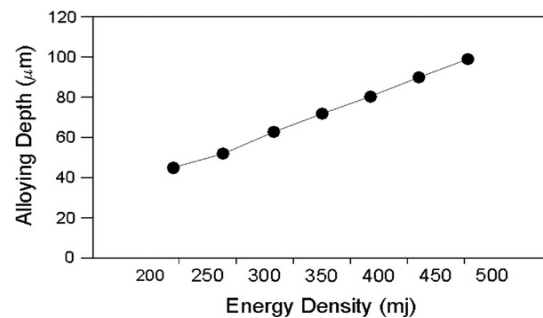
### 8.2.4.3 Ion implantation

The ion implantation is basically a post deposition surface treatment technique in which

ions of a material can be implanted into the coating, thereby transforming its physical properties. It has several advantages such as surface hardening of the material, reduced friction, increased fatigue, surface treatment with no rise in temperature (cold metallurgy), no geometric distortion, preservation of the state of the surface (e.g., super finishing) and its mechanical characteristics like low temperature tempered steel. Chang [80] in his research work examined ions of titanium that are implanted in EN-P coating developed over stainless steel in order to enhance its corrosion resistance characteristics.

### 8.2.4.4 Nitridation

Nitridation is a process through which heat treatment of a material in the presence of nitrogen atmosphere. Vitry et al. [81] found an increase of up to 1500HV<sub>100</sub> in micro-hardness of Ni–P coatings subjected to vacuum nitridation.



**Fig. 7. Role of power density of laser on alloying depth [79]**

### 8.2.4.5 Heat treatment in active atmosphere

Metal heat treatments are the techniques applied to transform the physical and chemical characteristics of a material. According to the desired microstructure and relative characteristics, different kinds of heat treatment may be applied depending on the material treated. Heating profile, time at temperature and cooling rate are the most crucial steps of heat treatment. Throughout these phases, protective atmospheres are maintained that is divided into active and neutral atmosphere. The EN-P coatings have been subjected to heat treatment under neutral and active atmospheres, among which the later induced improved case hardness, wear resistance and lower friction coefficient [82].

#### 8.2.4.6 Corrosion

The most demanding requirement in oil pipes is to give protection against corrosive environments. EN coating is noble than steel and aluminum. It protects the substrate by giving a pore free barrier coating. Because of its amorphous nature in high phosphorus and passivity, the corrosion resistance of the coating is great and in many environments it is much better than pure nickel or chromium alloys. Alloys containing high P are more resistant to attack than those with lesser phosphorus contents [83] in neutral or acidic environments. Alloys consisting of low phosphorus (3–4%) are more resistant to stronger alkaline environments compared to the high phosphorus deposits. Heat treatment on EN starts forming nickel phosphide around 250°C, lessening the P content of the rest of the material. This lessens the corrosion resistance of the coatings. The Ni–B alloy coatings are less corrosion resistant than that of high phosphorus Ni–P alloys and this can also be presented by Table 3 [84].

In petroleum industry, long tubes were used for heat exchange. These pipes were made of stainless steel which is gradually taken over by EN plated steel as it is more cost effective than

stainless steel. However, electroless coating has many pin-holes due to hydrogen bubble evolution during electroless deposition. These pin-holes decrease the corrosion protection capability of the coating. Researchers figured that solution gel ceramic coating on EN deposit decreases the pin-holes on the surface and also enhances the wearing quality [85].

#### 8.2.5 Mechanical properties

The mechanical characteristics mainly depend on the phosphorus/boron content in the deposit. The coatings usually have high strength, limited ductility, and high modulus of elasticity. The ultimate tensile strength of commercial coatings exceeds 700 MPa and allows the coatings to withstand loading without damage [86]. Typical mechanical and physical properties of EN-P/B coating are shown in Table 4 [87].

##### 8.2.5.1 Ductility

Ductility and internal stress in the EN coatings are the major functions of coating composition. With lesser phosphorus deposits, tensile stresses of 15–45 MPa develop, due to the difference in thermal expansion between the deposits and the substrate. The high level of

**Table 3. Corrosion rate ( $\mu\text{m}/\text{year}$ ) of EN-P/Ni–B at 20°C [84]**

Environment	Ni-P (11 – 12 % P)	Ni-B (4 – 5 % B)
Acetic acid, glacial	0.8	84
Acetone	0.08	Nil
Aluminum Sulfate 27%	5	-
Ammonia, 25%	16	40
Ammonium nitrate, 20%	15	Very rapid
Ammonium Sulfate, saturated	3	3.5
Brine 3.5% salt, CO <sub>2</sub> saturated (95°C)	5	-
Calcium Chloride, 42%	0.2	-
Citric Acid saturated	7	42
Cupric chloride, 5%	25	-
Ethylene glycol	0.6	0.2
Ferric chloride, 1%	200	-
Formic Acid, 88%	13	90
Hydrochloric Acid, 5%	24	-
Hydrochloric Acid, 2%	27	-
Lactic Acid, 85%	1	-
Lead Acetate, 36%	0.2	-
Nitric Acid, 1%	25	-
Oxalic Acid, 10%	3	-
Phenol 90%	0.2	Nil
Phosphoric Acid, 85%	3	Very rapid
Sodium Carbonate Saturated	1	Nil
Sodium hydroxide, 50% (95°C)	0.2	-
Sodium Sulfate, 10%	0.8	11
Sulfuric Acid, 65%	9	-
Water acid mine, 3.3 pH	7	-

stress in these coatings encourages cracking and porosity. The structural change during heat treatment at temperature above 220°C leads to a volumetric shrinkage of EN deposits up to 6%. This enhances the tensile stress and decreases the compressive stress in the coating. Deposit stress can also be enhanced by the co-deposition of orthophosphates or heavy metals, as well as by the presence of excess complexing agents in the plating solution. Even small quantities of some metals can produce a severe increase in stress. High levels of internal stress also decrease the ductility of the coating [88]. Ductility of the EN-P coating also varies with composition. The co-deposition of composites will impact the ductility characteristics. For deposits in as-deposited condition with relatively high phosphorus content, coatings have a ductility of 1–1.5% (as elongation) [89].

**8.2.5.2 Tensile strength**

The tensile strength value of Ni–P deposits has low phosphorus deposit of value 450–550 M Pa. Heat treated Ni–P possesses weaker tensile strength than that of as-deposited one but its hardness enhances. Its value is reported to be 200–300 M Pa [89].

**8.2.5.3 Hardness**

Hardness of EN coatings in as-deposit and heat-treated conditions in respect of phosphorus/boron content are compared in Table 5 [90] below which is equivalent to many other hardened alloy steels.

Yan et al. developed a high hardness value of 910 HV0.1 of as-deposited Ni– P coating at 8% phosphorus content, by varying the ratio of lactic acid to acetic acid in the electroless bath, and high wear resistance was accordingly achieved [91] also shown in Fig. 8.

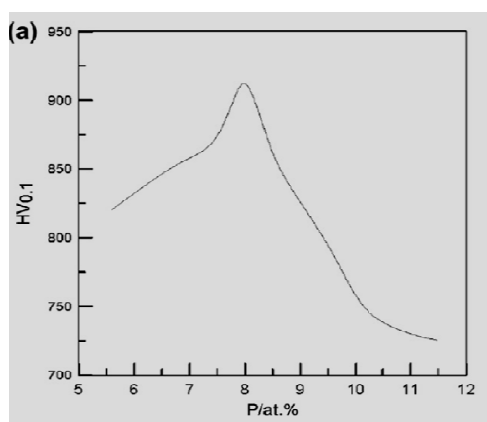
Researchers also figured out that hardness of electroless coating is seen to increase with the annealing temperature up to a certain temperature above where then the hardness is observed to decrease [92]. Ni–P, which is a supersaturated alloy in as-deposited state, can get stronger by precipitation of nickel phosphide crystallites with suitable heat treatments. The phosphides operate as barricades for dislocation movement, thereby improving the hardness further. However, the hardness of Ni–P films lowers down with excessive annealing because of the grain coarsening [93] leading to surface brittleness and improved dislocation propagation [94].

**Table 4. Physical and mechanical properties of EN-P coatings [87]**

Property	3-4% P	6-9% P	11-12% P	0.5-1% B	3-5% B
Structure	Microcrystalline	Mixed microcrystalline & amorphous	Amorphous	Crystalline	Mixed microcrystalline & amorphous
Internal Stress (MPa)	-10	+40	-20	+500	+110
Liquids (°C)	1275	1000	880	1440	1170
Density (gm/cm <sup>3</sup> )	8.6	8.1	7.8	8.6	8.25
Coefficient of thermal expansion(mm/m °C)	12.4	13	12	-	12.1
Electrical resistivity (ohm cm)	30	75	100	10	89
Thermal conductivity (W/cm K)	0.6	0.05	0.08	-	-
Specific heat (J/Kg K)	1000	-	460	-	-
Magnetic coercivity (A/m)	10000	110	0	-	-
Tensile Strength (MPa)	300	900	800	-	110
Ductility (elongation) (%)	0.7	0.7	1.5	-	0.2
Modulus of elasticity (G Pa)	130	100 - 120	170	-	120

**Table 5. Hardness (HV0.1) of EN coatings [90]**

Phosphorous/Boron content	As-deposited	Heat Treated (400 °C / 1 h)
2-3 % P	650	1200
6-9 % P	620	1100
10-12 % P	520	1050
1-5 % B	700	1280
5-10 % B	570	1120

**Fig. 8. Effect of phosphorous content on micro-hardness of Ni-P coating [91]**

#### 8.2.5.4 Solderability

EN-P can be easily soldered in comparison to the boron deposits. It is used in electronic application to promote soldering such light metals as aluminum. Rosin mildly activated (RMA) flux along with conventional Sn-Pd solder is most common. Pre-temperature of the component around 100°C enhances the ease and pace of joining and this flux is just for wetting the coating surface [95].

#### 8.2.5.5 Wear resistance

Electroless nickel is mostly serviced in wear applications in the precipitation-hardened condition. The coatings are characterized by greater hardness and wear resistance. They are even further enhanced by heat treatment. Heating for 1 h at 400°C leads to optimum hardness, which is comparable to 'hard' chromium deposits in hardness and wear resistance [95,89,91]. Long term treatments (30–40 weeks) at temperatures around 290°C can result in hardness values of 1700–2000 HV0.1 [96,97]. These low-temperature treatments lead to a finer dispersion of nickel boride than do higher temperatures and in the formation of iron borides (such as Fe<sub>2</sub>B and Fe<sub>3</sub>C<sub>0.2</sub>B<sub>0.8</sub>) within the coating, when the substrate is ferrous alloy.

Fig. 9 shows the low phosphorus is better than high phosphorus and heat treated Ni-B has comparable wear resistance to hard chrome [89,84,98].

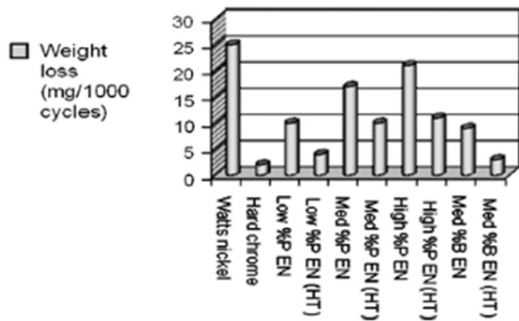
Sahoo examined the optimizing of the coating process parameters for the minimum wear based on L<sub>27</sub> Taguchi orthogonal design with four process parameters, i.e. bath temperature, nickel concentration source solution, RA concentration and annealing temperature. The findings in the report reveal that the annealing and bath temperatures have the most significant impact in controlling wear properties. The interaction of bath temperature and concentration of nickel source solution has some significant impact [99,100]. Wear performance on self-mated groups of Ni, Cu and Ni-P coatings have been studied by EN-P coating onto the friction surfaces. The EN-P coating during friction improves the growth of transfer particles in Cu/Cu and Ni/Ni rubbing systems. The particles were harder than the original surface because of the incorporation of coating material. This is the reason of the increment of the growth of transfer particles encompassed with the coating during friction [101]. The most popular use of EN for both corrosion and wear resistance is in valves that control the flow of oil and gas pipelines [102].

#### 8.2.5.6 Frictional properties

These also diversify with phosphorus/boron contents and with heat treatment. They are similar to those of chromium. The phosphorus content provides natural lubricity, which can be very advantageous for applications including plastic molding. The coefficient of friction for EN /boron versus steel is 0.12–0.13 for lubricated conditions and 0.43–0.44 for un-lubricated conditions [103]. Coefficients of friction of chromium coating, EN in the as-deposited condition and after heat treating at 400 °C (EN400) and at 600°C (EN600) are listed in Table 6 [104]. The counter surfaces were diamond and plain carbon steel. The coefficients of friction of the EN are greater than those of the chromium deposits.

**Table 6. Coefficients of friction of chromium versus EN [104]**

Coating	Counter faced diamond	Counterface plain C steel (080M40)
Cr	0.03-0.04	0.81-0.88
EN	0.18	0.96
EN400	0.30	0.95
EN600	0.06	0.90

**Fig. 9. Wear resistance of various coatings [89,84,98]**

## 9. VARIANTS OF ELECTROLESS COATING

### 9.1 Electroless Alloy Coating

EN-P coatings are observed to be suitable in room temperature applications but very few examiners have worked on their high temperature use. In many fields like aerospace and automobile, the coating may be subjected to operation at elevated temperatures. Hence, research on the characteristics of EN coatings at elevated temperature is much relevant. Hardness value of as-deposited coated samples tested at 550°C is observed to be higher by about 70% because of the high temperature transformation from the Ni-P amorphous phase to a mixture of hard Ni<sub>3</sub>P and nickel which usually occurs for the case of heat treatment [105]. Creation of an oxide layer on contacting surfaces is the major reason for as-deposited EN-P 10% coatings to illustrate the greatest wear resistance and the lowest friction coefficient in the wear test at 550°C. With heat treatment, wear resistance of EN-P 10% coating got enhanced at room temperature wear test due to the crystallized structure, though it exhibits an opposite nature in the wear test at 550°C [105].

### 9.2 EN Composite Coating

A commixture of hard particles (e.g. SiC, WC, ZrO<sub>2</sub>, diamond, Al<sub>2</sub>O<sub>2</sub>, Si<sub>3</sub>N<sub>2</sub>, BN and TiO<sub>2</sub>) and

dense lubricants (e.g. PTFE, graphite, MoS<sub>2</sub> and carbon nanotube) into Ni-P matrix can augment the mechanical and tribological performances of Ni-P composite coatings. The hardened composite coating has a wear resistance of high order of magnitude compared to that of a traditional Ni-P coating (heat-treated in the same conditions, i.e. for 1 h at 400°C) in room temperature test. However, very limited data on the impact of temperature on the tribological conduct of the Ni-P composite coatings are available. Applications of heat treatment to other composite coatings are available in the literatures. Ni-P-SiC composite coatings help to enhance its wear resistance by 135% in comparison to that of as-deposited condition due to the precipitation hardening [106]. León et al. [107] examined the high-temperature tribological behavior of Ni-P-BN autocatalytic coatings deposited on AISI 316L stainless steel and observed that the incorporation of solid lubricant BN did not lower the friction and wear. The friction coefficient and wear of the composite coatings is observed to improve with increasing operation temperature due to the change in wear mechanism.

A comparison between alloy and composite coating with respect to micro hardness and wear rate is shown in Fig. 10 [108] respectively. High temperature wear rate of Ni-P coating is observed to be about 10 times more than room temperature wear, but this value decreases by about two folds for nano crystalline Ni-P-Ag composite coating.

### 9.3 EN Nano Coating

EN nano coatings are described as to have either the thickness of the coating or the second phase particles will disperse into the Ni-P matrix in the range of nano-level. The workability to incorporate the fine second phase (in nano size range) particles such as SiO<sub>2</sub>, CNT, ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Al<sub>3</sub>Zr, hexa ferrites, ferrites ZnO, Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> within a metal/alloy matrix has instituted a new generation of EN-P nano composite coatings. In the last decade, many examiners have synthesized many EN-P nano composite



coatings. Among them, the combinations that have received considerable attention is SiC [109], CeO<sub>2</sub>, TiO<sub>2</sub> [110,111], Al<sub>2</sub>O<sub>3</sub>, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, ZnSnO<sub>3</sub>, ZnSiO<sub>3</sub> [112], single wall carbon nano tubes (SWCNTs) [113], and nanometer diamond (ND) [114]. In addition to this, either the EN-P deposition layer at nano level or on the nano size particles is also designated as EN-P nano coatings.

### 9.4 EN-P Nano Composite Coatings

EN-P deposits assimilated with nano-diamond particles was prepared and the mechanism is described [114]. Xiang et al. [115] came up with the findings that the nano sized diamond particles (0.52– 2.21 wt %) in the EN-P matrix changed the surface from bright and smooth to foggy and rough with nodular surface. In another research, Ni-P composite coatings were acquired by integrating two kinds of particles, SiC and Si<sub>3</sub>N<sub>4</sub>, to examine the impact of the type of particle both on the co-deposition process and on the coating characteristics (particles size ranging from 30 nm to 2 μm). It was seen that the growth mechanism of the metallic matrix was a lot more modified by the nano-particles than by the micron-sized particles [116].

An alkaline bath with in situ co-precipitation reaction has been formed successfully to deposit Ni-P-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/Al<sub>3</sub>Zr electroless coatings on three different substrate materials, commercial aluminum, low carbon steel and carbon fabric [117]. Second phase nano size (80 nm) Al<sub>2</sub>O<sub>3</sub> particles integrated with Ni-P matrix were formed and examined [118]. Furthermore, the impact of

particle size on the microstructure, hardness and corrosion resistance of EN-P-Al<sub>2</sub>O<sub>3</sub> composite coatings with the size of 50 nm, 0.3 μm and 1 μm has been examined.

Agarwala prepared to encompass the nano barium hexa ferrites (BaZn<sub>2-y</sub>Co<sub>y</sub>Fe<sub>16</sub>O<sub>27</sub>) into EN-P matrix as barium hexa ferrite is a crucial magnetic material, usually applied as permanent magnet, magnetic recording media and microwave absorbers. The findings indicate that this EN-P nano composite coating has good microwave absorption characteristics [119].

Dong et al. reported that the SiO<sub>2</sub> nanoparticles were capable for great enhancement of the mechanical properties of EN-P coating, improving the micro-hardness (after approx 400 °C treatment) and wear resistance [120]. The volume of SiO<sub>2</sub> (2 wt.%) nano-particles (20 nm in size) co-deposited in the Ni-P (8 wt.%) matrix enhanced the corrosion resistance of coatings in salty atmosphere [121]. EN-P deposit with inorganic fullurene-WS<sub>2</sub> nanoparticles has increased wear resistance under oil lubricated conditions, which is superior to Ni-P, Ni-P-2H-WS<sub>2</sub> and Ni-P graphite deposits. This is because of their ability to act as spacers between the asperities of two mating metal surfaces [122].

Carbon nanotubes (CNT) (12 vol. %), when fused in an EN-P matrix, improve the wear resistance in both asphalted and heat-treated conditions [123], better than that of EN-P-SiC and Ni-P-graphite deposits. CNT provides a low coefficient of friction, when integrated with the EN-P matrix [122,124].

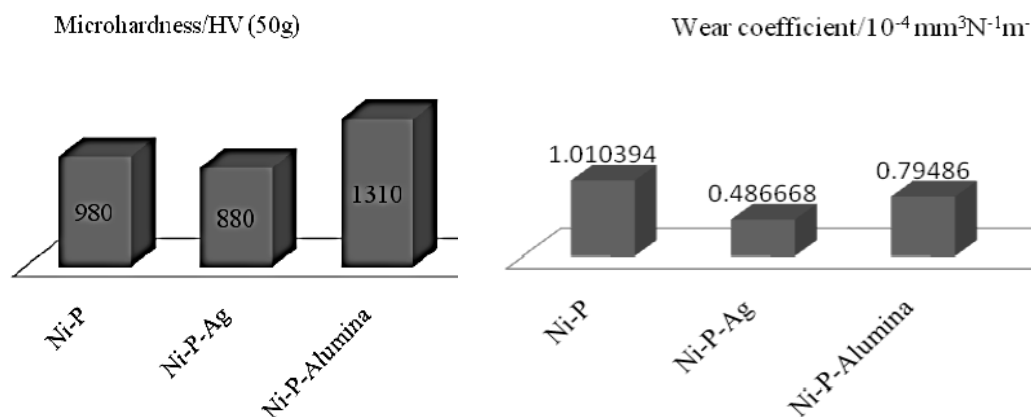


Fig. 10. Comparison between Ni-P (HT) and Ni-P-X coatings on the basis of hardness / high temperature [108]

## 10. FUTURE TRENDS

This review article gives a synopsis of the overall aspects of EN coatings in particular and organic/powder coatings in general, examining the coating developments in the oil and gas industry. In particular, it reflects upon the methods of formation of EN-P, poly alloys, composite coatings, nano coatings and their impact on coating characteristics, applications and their latest developments are less focused in the arena of oil and gas where else for organic and powder coatings the future is brighter.

In future, new alloys added with EN coating may effectuate new benefits and properties. Work needs to be done on enhancing the plating of difficult substrates (i.e., aluminum and magnesium) that need thick and eco-friendly coatings for some applications, and lessening the chemical usage and cost. In addition, gaining maximum efficiency from the bath is more crucial in future. Lowering the prices of electroless plating and minimizing the bath wastage, greener plating technology will be more attractive.

EN composite coatings have a potential of a bright future for wear-resistant or self-lubricating coatings and other special treatments. In future, new composite material may fulfill new benefits and property. With the arrival of automatic controllers and more advanced processing technology, poly alloys and composites may establish themselves as the next frontier of electroless technology. The composite coatings can give an excellent layer of coating consisting of nickel and other components to be used for oil and gas industry at exalted temperature.

The characteristics of EN coatings are constantly refined by the right surface treatments (heat, laser, etc.) and the incorporation of various elements (copper, tungsten, etc.) and particles (SiC, TiO<sub>2</sub>, etc.) by the several examiners to suit the various applications. The future of electroless plating will depend on the newer needs and applications, as well as transformations in plating technology.

## 11. CONCLUDING REMARKS

From the present review, it can be observed that organic/powder and EN coatings have come forward as suitable coating techniques that can be used in various fields. Their characteristics such as hardness, low friction, wear resistance and corrosion resistance have resulted in their

utilization in tribological applications. Properties such as, the uniform deposition and the ability to coat any materials, have served as an added advantage to their application in various areas. The benefits of modifying the characteristics of EN coatings by the right surface treatment (heat treatment, laser treatment, etc.) and the incorporation of various elements and particles have been employed by various investigators to analyze the feasibility of these coatings for various applications. The review reports that the electroless coatings are mainly applied for wear resistance and corrosion resistance operations.

Operations at exalted temperatures are usually linked with changes in the microstructure of the coating which could lead to grain softening phenomenon leading to demoted performance of the coating. Therefore it is concluded that the present article summarizes the characteristics of EN in totality. However, in some specific application areas such as oil and gas industry, quite insufficient research effort is done. With the demanding technological advancement, in the future more concentrated and elaborated investigations on the performance of several EN coatings in oil and gas field will be needed.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Science Media Center of Canada, the engineering science of oil pipelines; 2011.
2. U.S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration, ops.dot.gov/stats/stats.htm, report as of Oct 30; 2000.
3. Lekan Taofeek Popoola. Corrosion problems during oil and gas production and its mitigation. International Journal of Industrial Chemistry; 2013. Available:<http://www.europipe.com>
4. John F Kiefner. Oil pipeline characteristics and risk factors: Illustrations from the Decade of Construction, American Petroleum Institute's Pipeline Committee publication; 2001.
5. Peabody AW. Control of pipeline corrosion, 2<sup>nd</sup> edition; 2001.
6. NACE Standard RP0169-96 Section 5, characteristics of protective coatings. NACE international, the corrosion society, ISBN 1-57590-092-0.

7. Sorensen PA, Kiil S, Dam-Johansen K, Weinell CE. Anticorrosive coatings: A review. *J. Coat. Technol. Res.* 2009;6(2): 135–176.  
DOI: 10.1007/s11998-008-9144-2
8. Masterbond coatings, Protective epoxy coatings for oil and gas pipelines, New Jersey USA.
9. New Challenges and Developments in Pipeline Coatings [Article] / auth. Guan Shiwei William/ North American Pipelines. January/February 2010.  
Available:[www.napipelines.com](http://www.napipelines.com)
10. Masterbond adhesive sealant coatings. Available:<http://www.masterbond.com/articles/chemical-and-heat-resistance-protective-epoxy-coatings-oil-and-gas-pipelines> [on line accessed]
11. Westood J. Macro factors driving the global oil and gas industry and the subsea pipelines sector. Toronto, Canada; 2011.
12. Mallory G, Hajdu J. American Electroplaters and Surface Finishers Society, Orlando. 1990;3:6.
13. Riedel W. Electroless nickel plating, Finishing Publications Ltd, Stevenage, Hertfordshire, UK; 1991.
14. Muraliraja R, Sendilkumar D, DRR. Prediction and supplementation of reducing agent to improve the coating efficiency and wear behavior of electroless Ni-P plating. *Int. J. Electrochem. Sci.* 2015;10:5536–5547.
15. Puff TA. FBE Serves a Broad Market, *Harts Pipeline Digest.* 1996;20-25.
16. Ward DK, Moore EM, Hawkins PJ. External and internal pipeline coatings in Arabian Gulf Area, Proceedings 5th International Conference on Internal and External Protection of Pipes, Innsbruck; 1983.
17. Amir Samimia, Soroush Zarinabadi. An analysis of polyethylene coating corrosion in oil and gas pipelines. *Journal of American Science.* 2011;7(1):1032-1036.
18. Gaillard G, Bouliez JL. How Fusion-Bonded epoxies protect pipeline: Single- and dual-layer systems. *Journal of Protective Coatings and Linings;* 2010.
19. J.K. Prattand M.L. Mallozzi, The development of new FBE products, *Journal of protective coatings and linings,* 2010.
20. Patterson M, Drew S, Boerschel V. The development of a mid-Tg coating suitable for application on high temperature pipelines. *Journal of Protective Coatings and Linings;* 2010.
21. Amadi SA, Ukpaka CP. Performance evaluation of anti-corrosion coating in an oil industry. *Landmark Research Journals, Agriculture and Soil Sciences (LRJASS).* 2014;1(5):070-081.
22. Edmondson SJ. Development of a new range of FBE Coatings. NACE International 05026, Corrosion. 2005;3-7. Houston, Texas.
23. Fabio Aguirre, Don Kirkpatrick. Accelerated aging of fusion bonded epoxy coatings, Dow Coating Materials and Chemical Company Freeport, Texas, 77541 USA; 2008.
24. Shiwei William Guan. New challenges and developments in pipeline coatings. *Journal of North American Pipelines.* 2010;30-33.
25. Makanjuola Oki, Adeolu Adesoji Adediran, Paul A, Anawe L. Corrosion monitoring in the oil pipeline industry. *Journal of Multidisciplinary Engineering Science and Technology (JMEST).* 2015;2(1). ISSN: 3159-0040
26. Alan Kehr J, David G. Enos, FBE, a foundation for pipeline corrosion coatings. NACE Store - 00757 FBE; 2009.
27. Alan Kehr J, Sam Attaguile, Mark Smith. New technology helps develop coatings for high operating temperatures pipelines. *3M;* 2013.
28. Valérie Sauvart-Moynot, Serge Gonzalez, Jean Kittel. Self-healing coatings: An alternative route for anticorrosion protection. *Progress in Organic Coatings.* 2008;63:307–315.
29. Mathiazhagan A, Rani Joseph. Nanotechnology - A new prospective in organic coating – Review. *International Journal of Chemical Engineering and Applications.* 2011;2(4):
30. Wurtz A. Ann. Etudes sur l'Albumine et sur la Fibrine, Phd thesis, *Chim. et Phys.* 1844;3:11.
31. Breteau P. Bull. electroless plating: Fundamentals and applications. *SOC. Chim.* 1911;9.
32. Roux FA. The evolution of a process: Fifty years of electroless nickel Mandich NV, zp2.y HBM and G. Electrochemical A. Krulik & Engineering Co., Lansing, Ill. /w Applied Electroless Concepts, El Toro, Calif.
33. Brenner A, Riddell G. J. Res. Electroless plating *Nat. 8ur. Std.* 1946;37(31):ibid-39,385.  
Available:[http://www.tau.ac.il/~chemlaba/Files/Electroless/12777\\_01.pdf](http://www.tau.ac.il/~chemlaba/Files/Electroless/12777_01.pdf)

34. Baudrand DW. Advantages of electroless nickel plating of hybrid. U.S. Patent. 1978;4,091,128.
35. Lanzoni et al. Frontiers in materials science. Indian Academy of Science, Bangalore. 1997;480.
36. Jothi Sudagar, Jianshe Lian, Wei Sha. Electroless nickel, alloy, composite and nano coatings – A critical review. Journal of Alloys and Compounds. 2013;571:183–204.
37. Elansezhian R, Ramamoorthy B, Kesavan Nair P. Effect of surfactants on the surface roughness, hardness and microstructure of electroless (Ni-P) coatings. Inderscience Publishers. International Journal of Surface Science and Engineering. 2008;2:179-189.
38. Woo-Jae Cheong, Ben L Luan, David W Shoe Smith. The effects of stabilizers on the bath stability of electroless Ni deposition and the deposit. Journal of Applied Surface and Science. 2004;229: 282-300.
39. Agarwala RC, Vijay Agarwala. Electroless alloy/composite coatings: A review. Sadhana-a. 2003;28(Parts 3 & 4):475–493.
40. Elansezhian R, Ramamoorthy B, Kesavan Nair P. The influence of SDS and CTAB surfactants on the surface morphology and surface topography of electroless Ni-P deposits. Elsevier. Journal of Materials Processing Technology. 2009;206:233-244.
41. Muraliraja R, Elansezhian R. Influence of nickel recovery efficiency on crystallinity and microhardness of electroless Ni-P coatings and optimisation using Taguchi technique. 2015;93(3):126-132. Maney Online Publishing.
42. Elansezhian R, Ramamoorthy B, Kesavan Nair P. Effect of surfactants on the mechanical properties of electroless (Ni-P) coating. Elsevier Surface and Coating Technology Journal. 2008;203:709-712.
43. Sanjib Kundu, Suman Kalyan Das, Prasanta Sahoo. Properties of electroless nickel at elevated temperature-a review, Procedia Engineering 2014;97:1698–1706.
44. Agarwala RC, Agarwala V. Electroless alloy/composite coatings: A review. Sadhana. 2003;28(3–4):475–93.
45. Anik M, Korpe E, Sen E. Effect of coating bath composition on the properties of electroless nickel–boron films. Surf Coat Technology. 2008;202(9):1718–27.
46. Ying HG, Yan M, Ma TY, Wu JM, Yu LQ. Effects of NH<sub>4</sub>F on the deposition rate and buffering capability of electroless Ni-P plating solution. Surf Coat Technology. 2007;202(2):217–21.
47. Delaunois F, Petitjean JP, Lienard P, Jacob-Duliere M. Autocatalytic electroless nickel–boron plating on light alloys. Surf Coat Technol. 2000;124(2–3):201–9.
48. Parker K, Recent advances in electroless nickel deposits. 8th Inter finish Conference Basel; 1972.
49. Baldev Raj, Sankara Rao. Frontiers in material sciences. Indian Academy of sciences, Bangalore, Universities Press India Limited.
50. Elansezhian R, Ramamoorthy B, Kesavan Nair P. Study on characterization and influence of surfactants on adhesion and coating thickness of electroless Ni-P deposits. Inderscience Publishers. International Journal of Microstructure and Materials Properties. 2012;7:77-93.
51. Elansezhian Rasu. Study on structural characterization of surfactants influence on electroless Ni-P deposits. Science Domain International. British Journal of Applied Science and Technology. 2014;5:1-10.
52. Elansezhian R, Ramamoorthy B, Nair PK. The influence of SDS and CTAB surfactants on the surface morphology and surface topography of electroless Ni-P deposits. J Mater Process Technol. 2009; 209(1):233–40.
53. Sudagar J, Lian JS, Jiang Q, Jiang ZH, Li GY, Elansezhian R. The performance of surfactant on the surface characteristics of electroless nickel coating on magnesium alloy. Elsevier. Journal of Progress in Organic Coatings. 2012;74:788-793.
54. Rasu Elansezhian. Effect of nano additives with surfactant on the surface characteristics of electroless nickel coating on magnesium-based composites reinforced with MWCNT. Advances in Tribology. 2013;10. Article ID 315965. Available:<http://dx.doi.org/10.1155/2013/315965>
55. Elansezhian Muraliraja. Effect of zwitterionic surfactant on tribological behavior of electroless plating. Maney Publishing. Journal of Surface Engineering. 2014;5:752-757.
56. Amir Ahmadi Ashtiani, SoheilaFaraji. The study of electroless Ni-P alloys with different complexing agents on Ck45 steel substrate. Arabian Journal of Chemistry. Received 3 August 2012; Accepted 21 May 2013.

57. Ashassi-Sorkhabi H, Rafizadeh SH. Effect of coating time and heat treatment on structures and corrosion characteristics of electroless Ni-P alloy deposits. *Surf Coat Technol.* 2003;176(3):318–26.
58. Hurk H, Jeong JH, Lee DN. Microstructures and crystallization of electroless Ni-P deposits. *Journal of Materials Science.* 1990;25:2573-2584.
59. Mallory GO, Hadju JB. *Electroless plating: Fundamentals and applications.* Orlando: AESF; 1991.
60. Gou Y., Huang W., Zeng R, Zhu YT. Recent progress in electroless ni coatings for magnesium alloys non ferr. *Metal. Soc.* 2010;20:s674.
61. Chen W, Gao W, He Y. Ni-P-TiO<sub>2</sub> Composite coatings on copper produced by sol-enhanced electroplating. *Surface Coating Technol.* 2010;204:2493.
62. Zhang JW, Hou LF, Xu BS. Transactions of materials and heat treatment, *Int. J. Electrochem. Sci.* 2015;10:1261–1273. 2010;31:137.
63. Correa E, Zuleta AA, Guerra L, Gómez MA, Castaño JG, Echeverría F, Liu H, Skeldon P. Measurement of mechanical properties of an electroless Ni-B coating using nano indentation. *Ind. Eng. Chem. Res.* 2012;51(22):7762–7768.
64. Xin SHU, Recent progress in electroless Ni coatings for magnesium alloys. *Int. J. Electrochem. Sci.* 2015;10:1261–1273.
65. Yan M, Ying HG, Ma TY. Improved micro hardness and wear resistance of the as-deposited electroless Ni-P coating. *Surf Coat Technol.* 2008;202(24):5909–13.
66. Vafaei-Makhsoos E, Thomas EL, Toth LE. Electron microscopy of crystalline and amorphous Ni-P electrodeposited films: In situ crystallization of an amorphous solid. *Metall. Trans.* 1978;9:1449–1460. (In English)
67. Lü Y., Wang Q, Zeng X, Ding W, Zhai C, Zhu Y. Recent progress in electroless Ni coatings for magnesium alloys. *Mat. Sci. Eng. A-Struct.* 2000;278:66.
68. León OA, Staia MH. Influence of heat treatment on tribological behavior of Ni-P autocatalytic coatings. 1999;15(5):391-394.
69. Srinivasan KN, Meenakshi R, Santhi A, Thangavelu PR, John S. Studies on development of electroless Ni-B bath for corrosion resistance and wear resistance applications. *Surf Eng.* 2010;26(3):153–8.
70. Riedel W. *Electroless nickel plating,* Finishing Publications Ltd, Stevenage, Hertfordshire, England (1991) and Thompson GE, *Wear.* 2013;305:115.
71. Michal Nováka, Dalibor Vojtěcha. Influence of heat treatment on tribological properties on EN-P coatings. *METAL.* 2009;19(21):5. Hradec Nad Moravicí.
72. Nava D, Dávalos CE, Martínez-Hernández A, Manríquez F, Meas Y., Ortega-Borges R, Pérez-Bueno J, Trejo G. Effects of heat treatment on the tribological and corrosion properties of electrodeposited Ni-P alloys. *Int. J. Electrochem. Sci.* 2013;8:2670–2681.
73. YaXu Jin. Characteristics of electroless nickel-phosphorus-potassium titanate whisker composite coating. *Advanced Materials Research.* 2012;472-475:70-73.
74. Zhou QJ, Zhao JQ, Nie F, Chu WY, Li JX, Qiao LJ. The effect of hydrogen on friction and wear of Ni-P electroless coating. *Wear.* 2009;266(7–8):810–3.
75. Garcia -Alonso MC, Escudero ML, Lopez V. The corrosion behavior of laser treated Ni-P alloy coatings on mild steel. *Corrosion Science.* 1996;38(3):515-530.
76. Zhuangyi Liu, Microstructure and corrosion performance of laser-annealed electroless Ni-W-P coatings. *Surface and Coatings Technology.* 2010;204(s 9–10):1549–1555. DOI: 10.1016/j.surfcoat.2009.09.074
77. Liu1 H, Guo RX, Bian JS, Liu Z. Effect of laser-induced nano crystallization on the properties of electroless Ni-P/Ni-W-P duplex coatings. *Crystal Research and Technology.* 2013;48(2):100–109.
78. Gordani GR, ShojaRazavi R, Hashemi SH, Isfahani ARN. Laser surface alloying of an electroless Ni-P coating with Al-356 substrate. *Opt Lasers Eng.* 2008;46(7): 550–7.
79. Razavi RS, Salehi M, Monirvaghefi M, Gordani GR. Laser surface treatment of electroless Ni-P coatings on Al356 alloy. *J Mater Process Technol.* 2008;195(1–3): 154–9.
80. Chang YY, Wang DY. Corrosion behavior of electroless nickel-coated AISI 304 stainless steel enhanced by titanium ion implantation. *Surf Coat Technol.* 2005; 200(7):2187–91.
81. Vitry V, Delaunois F, Dumortier C. Nitridation treatments to improve the hardness and mechanical properties of electroless nickel-boron deposits. 15<sup>th</sup> IFHTSE – International Federation for Heat

- Treatment and Surface Engineering Congress, Vienna. 2006;25,506–11.
82. Zangeneh K, Monir-Vaghefi SM. Improvement of tribological behavior of thin Ni–P layers on 4140 steel by treatment in active atmosphere. 29th ed. 2005;327–30.
  83. Gould AJ, Boden PJ, Harris SJ. Phosphorus distribution in electroless nickel deposits. *Surf. Techn.* 1981;12(1): 93–102.
  84. Baudrand D. Electroless nickel plating, ASM Handbook, vol. 5, Surface Engineering, ASM International, Materials Park, OH. 1994;290–310.
  85. Guglielmi N. + Author ... 4, 1972. © 1972 ECS - The electrochemical society ... preparation and photo electrochemical property of PbO<sub>2</sub>-TiO<sub>2</sub> nano composite. *Electrodes J. Electrochem. Soc.* 1972; 119(8):1009-1012.
  86. Song H, Weng L-Q. Embrittlement of a Cr-Mo low-alloy steel due to low-temperature neutron irradiation. *Acta Metall. Sinica (English Letters)*. 2006;19:20-26.
  87. Keong KG, Sha W. Crystallisation and phase transformation behaviour of electroless nickel-phosphorus deposits and their engineering properties. *Surf. Eng.* 2002;18:329–343.
  88. Agarwala RC, Agarwala V, Sadhana. Electroless alloy/composite coatings: A review. *Springer*. 2003;28:475–493.
  89. Parker K. Progress of electroless amorphous and nanoalloy deposition: A review. *Plat. Surf. Finish.* 1981;68(12):71–76.
  90. Gawrilov GG. Chemical (Electroless) nickel plating, Portcullis Press, Red hill, England; 1979.
  91. Keong KG, Sha W, Malinov S. Effect of phosphorous content on micro-hardness of Ni–P coating. *Surf. Coat. Technol.* 2003; 168:263–274.
  92. Yan M, Ying HG, Ma TY. Characterization and corrosion performance of multilayer nano nickel coatings on AZ31 magnesium alloy. *Surf. Coat. Technol.* 2008;202:5909–5913.
  93. Oraon B, Majumdar G, Ghosh B. Improving hardness of electroless Ni–B coatings using optimized deposition conditions and annealing. *Mater Des.* 2008;29(7):1412–8.
  94. Palaniappa M, Seshadri SK. Friction and wear behavior of electroless Ni–P and Ni–W–P alloy coatings. *Wear.* 2008;265(5–6): 735–40.
  95. Dong D, Chen XH, Xiao WT, Yang GB, Zhang PY. Preparation and properties of electroless Ni–P–SiO<sub>2</sub> composite coatings. *Appl Surf Sci.* 2009;255(15): 7051–5.
  96. Krishnan KH, John S, Srinivasan KN, Praveen J, Ganesan M, Kavimani PM. A study on the microstructure and phase transformation of electroless nickel deposits. *Metall. Mater. Trans. A.* 2006;37: 1917–1926.
  97. Gawrilov GG. Chemical (Electroless) Nickel Plating, Portcullis Press, Redhill, England, UK; 1979.
  98. Dervos CT, Novakovic J, Vassiliou P. *Mater. Lett.* 2004;619–623. Dennis K, Such TE. Nickel and chromium plating, Woodhead Pub Ltd; 1993.
  99. Sahoo, Mater. Des. Wear behavior of electroless Ni-P coatings and optimization of process parameters using Taguchi method. *Procedia Engineering.* 2009;30: 1341–1349.
  100. Sahoo P. Wear behaviour of electroless Ni–P coatings and optimization of process parameters. *J. Phys. D Appl. Journal of Phys.* 2008;41:095305.
  101. Hiratsuka K, Abe Y, Kawashima S. Effect of in-situ electroless plating on friction and wear of metals. *Wear.* 2003;255:910–916.
  102. Mallory GO, Hajdu JB. *Electroless plating: Fundamentals and Applications*, William Andrew; 1990.
  103. Randin JR, Hintermann HE. Electroless nickel deposited at controlled pH-mechanical properties as a function of phosphorus content. *Plating.* 1967;54:523–532.
  104. Gawne DT, Ma U. Friction and wear of chromium and nickel coatings. *Wear.* 1989;129:123–142.
  105. Masoumi F, Ghasemi HR, Ziaei AA, Shahriari D. Tribological characterization of electroless Ni –10% P coatings at elevated test temperature under dry conditions. *Int. J. Adv. Manuf. Technol.* 2012;62:1063-1070.
  106. Staia MH, Conzoño A, Cruz MR, Roman A, Lesage J, Chicot D, Mesmacque G. Wear behavior of silicon carbide/electroless nickel composite coatings at high temperature. *Surf. Eng.* 2002;18(4):265-269.
  107. Leon OA, Staia MH, Hinterman HE. High temperature wear of an electroless Ni-P-

- BN (h) composite coating, Surf. Coat. Technol. 2003;163-164:578-584.
108. Alirezaei S, Monirvaghefi SM, Saatchi A, Vrgen M, Motalebzadeh A. High temperature friction and wear behaviour of Ni-P-Ag-Al<sub>2</sub>O<sub>3</sub> hybrid nano composite coating, Trans. Inst. Met. Finish. 2013; 91(4):207-213.
  109. Jiaqiang G, Lei L, Yating W, Bin S, Wenbin H. A study of electroless copper-phosphorus coatings with the addition of silicon carbide (SiC) and graphite (Cg) particles Surf. Coat. Technol. 2006;200: 5836–5842.
  110. Balaraju JN, Sankara Narayanan TSN, Seshadri SKJ. Evaluation of the corrosion resistance of electroless Ni-P and Ni-P composite coatings by electrochemical impedance spectroscopy. Solid State Electrochem. 2001;5:334–338.
  111. Jin HM, Jiang SH, Zhang LN. Chin. Chem. electroless nickel, alloy, composite and nano coatings – A critical review. Lett. 2008;19:1367–1370.
  112. Tao P, Mei-Hua M, Fei-Bo X, Xin - Quan X. Electronic structure and optical properties of ZnSiO<sub>3</sub> and Zn<sub>2</sub>SiO<sub>4</sub>. Appl. Surf. Sci. 2001;181:191–195.
  113. Yang Z, Xu H, Shi YL, Li MK, Huang Y. Electroless composite coating of Ni-P-carbon nanotubes on magnesium powder. Li HL, Mater. Res. Bull. 2005;40:1001–1009.
  114. Petrova M, Noncheva Z, Dobrev E. Electroless deposition of Ni-P composite coatings containing kaolin nanoparticles. Trans. Inst. Met. Finish. 2011;89:89–94.
  115. Xiang YW, Zhang JY, Jin CH. Molecular cytogenetic characterization of electroless plating and surface finishing of composite coatings. Plat. Surf. Finish. 2001;88(2):64–67.
  116. Sarret M, Müller C, Amell A. Electroless Ni-P coatings: Preparation and evaluation of fracture toughness and scratch hardness. Surface Coating Technol. 2006;201:389–395.
  117. Agarwala RC, Sharma R. EMI reduction, Radar/Microwave absorbing nano composite materials for L, C, X and Ku in X-band. Met.-Org. Nano-Met. Chem. 2008; 38:229–236.
  118. Agarwala RC, Agarwala V, Sharma R. Mechanical preparation of tio<sub>2</sub> nanoparticles and their incorporation in electroless Ni-P coatings. Met.-Org. Nano-Met. Chem. 2006;36:493–515.
  119. Agarwala RC. Pramana, electroless nickel, alloy, composite and nano coatings – A critical review. 2005;65:959–965.
  120. Dong D, Chen XH, Xiao WT, Yang GB, Zhang PY. Preparation and properties of electroless Ni-P-SiO<sub>2</sub> composite coatings. Appl. Surf. Sci. 2009;255:7051–7055.
  121. Rabizadeh T, Allahkaram SR. Porosity measurement of electroless Ni-P coatings reinforced by CNT or SiC particles. Mater. Des. 2011;32:133–138.
  122. Chen WX, Tu JP, Xu ZD, Tenne R, Rosenstveig R, Chen WL, Gan HY. Inorganic nano materials from nanotubes to fullerene-like nanoparticles, fundamentals and applications. Adv. Eng. Mater. 2002;686–690.
  123. Chen WX, Tu JP, Xu ZD, Chen WL, Zhang XB, Cheng DH. Tribological properties of Ni-P-multi walled carbon nanotubes electroless composite coating. Mater. Lett. 2003;57:1256–1260.
  124. Moonir-Vaghefi SM, Saatchi A, Hejazi J. Electroless Ni-P composite coatings. Journal of Applied Electrochemistry. 2003; 807–816. Kluwer Academic Publishers
  125. Mirza MM, Elanzeshian Rasu, Anjali Desilva. Corrosion protection of steel pipelines used in oil and gas industry of Oman. BJUST 20077, 2015;11(6):1-18.
  126. Mirza MM, Elanzeshian Rasu, Anjali Desilva. Influence of nano additives on protective coatings for oil pipe lines of Oman. IJCEA. 2016;7(4).

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