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Corrosion Prevention of Metals via Electroless Nickel Coating: A review

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Abstract. Electroless coating is a chemical process that involves an autocatalytic response of the constituents in an aqueous mixture. It also involves multiple simultaneous reactions, with non-galvanic excitation, that causes the formation of thin film layers i.e. the coating, on the substrate of the material. The reduction of metallic ions required to coat the surface of the metal occurs due to the reducing agent in that same compound, which supplies an intrinsic potential difference to allow current flow. This follows by the need for the cations of the deposition metal to be reduced by electrons receiving them at the substrate, electrons which the reductant also donates to this surface thereby undergoing oxidation. The most generally used electroless plating technique is the electroless nickel plating method, which involves the deposition of un-crystallized nickel alloy on the substrate, with even thickness regardless of the shape and form of the material due to its independence on current. The paper reviews the tribo-corrosion resistances, mechanical properties and conductivity of electroless nickel coatings.

Keywords: Electroless, Coatings, Metals, Ions, Deposition.

1 Introduction

Corrosion is natural and familiar phenomenon associated with the chemical degradation of materials and their properties as a result of an electrochemical reaction with their environment; the corrosion of metals is inevitable and while usually associated with generally only metals, it is a common factor to all materials [1]. It is not just a natural occurrence without impact, it is a disastrous occurrence with devastating blows to the growth of humanity and various nations, as it is an economic hurdle causing the world a global deficit of nearly \$4 trillion annually [2].

1.1 Forms of Corrosion

It has many forms such as:

- Galvanic corrosion: Different metals possess different potentials to corrode when placed in contact, therefore, electrons tend to flow from the more reactive metal to the less reactive, forming a galvanic couple: This emulates the anodic and cathodic sites respectively. This method of corrosion usually speeds up the process of corrosion for the anodic metal, and reduces the process of corrosion for the cathodic metal, with the acting power being directly proportional to the electro-chemical potential difference between the dissimilar metals. Theoretically, galvanic corrosion can be eliminated by insulating any electrical contact between the substrate and other metals [3].
- Uniform corrosion: This type of corrosion occurs when the metal degradation occurs at a very similar rate aggregate on large areas of corrosion. Uniform corrosion takes place in a homogenous environment. It is also called general corrosion, and is a corrosion process dominated by uniform thinning which develops steadily without notable localized attacks. It possesses two stages of its mechanism, the initial stage where the substrate is being attacked, and the second stage of propagation [4].

- Pitting corrosion: Pitting corrosion comes in the form of pits/small holes in metals and is common in metals above pitting potential, passive metals such as steel buried in soil [2]. The basic pitting formation consists of three phases [4], first which is pit nucleation which forms a bare surface of substrate exposed to the environment, second is a dissolution of the underlying metal, and third is pit propagation.
- Erosion corrosion : Erosion corrosion is a set range of corrosion phenomenon that describes situations dominated by oxidation reaction to those dominated by physical damage and wear, with more in-between occurrences which combine the two [5]. Erosion modelling is applied to the design of material in contact with flowing fluids with focus on the two main mechanisms of the corrosion type, cutting and deformation [6].

1.2 Corrosion Protection

To curb the effects of corrosion, various techniques have been invented with the aim of stifling its activation process, through restricting or eradicating elements of its cause of propagation, these methods involve: Coating the surface likely to corrode; proper material selection; application of inhibitive mediums to the corrosive media; insulation of conductive sections of the material; or finally, through proper equipment design [7]. To prevent corrosion and its effects, various methods of corrosion protection are utilized: Corrosion protection includes all steps, processes and standard techniques used as a means to prevent the corrosion of a material, and the damage that occurs thereof. Protection against corrosion consists of a manifold of techniques and ideas that aim to use the knowledge of the electrochemical action of corrosion against itself. These techniques border around removing the elements that enable the electrochemical reaction - removing these elements/materials, cuts the effect of corrosion short, or reduces its rate significantly. Methods utilized in protection of metals against the electrochemical effects of corrosion:

- Material selection for design and application;
- Surface coating;
- Application of Inhibitors;
- Proper system modelling;
- Electrical protection [1].

These methods aim at eliminating elements of corrosion or disconnecting these elements to restrict reaction with one another. The elements of corrosion include the anode, cathode and the conducting medium such as an electrolyte. Corrosion protection can be active or passive; Active protection is a means of corrosion protection that works by taking effective control of the process of corrosion, which could include the modelling of the system, material selection and general design. Passive protection on the other hand is a means of protection where corrosion is removed, or its rate reduced, by isolation of the material from the corrosive media through the application of inhibitive layers. Coating is a passive protection technique, and conditions that determine its nature are:

- The porosity of the coating;
- Adhesivity to substrate;
- Corrosion resistivity, chemical resistances and enhanced mechanical properties;
- Ductility [8].

2 Surface Coating Techniques

Surface coatings can be divided into metallic and non-metallic coatings. Non-metallic coatings can be either organic or non-organic.

- In-Organic Coatings: Inorganic coatings are created out of the occurrence of a galvanic or non-galvanic chemical reaction [9]. These serve their purpose by installing a thin film with better corrosion resistivity on the substrate. Methods of inorganic coating include oxidation, phosphating, enameling and cementation. Oxidation involves coating steel with an oxide film by heating at high temperatures in the presence of oxygen, chemical oxidation treatments with other chemical compounds or anodic oxidation in an electrolytic cell. Phosphating involves coating steel with a layer of iron phosphate. Enameling

consists of coating with a glass layer by dipping the metal in a suspension of powdered glass followed by high temperature melting of the glass on the metal surface. Cementing or cement coating is usually applied to the inside of steel pipes carrying waste water. Metallic coating can also be described as a form of inorganic coating [10].

- **Organic Coatings:** Organic coatings are the oldest and most widespread method of corrosion prevention on the surface of metals, this is as a result of their make-up. Organic coatings consist of ingredients derived from natural sources usually rich in carbon and its compounds, with properties such as chemical inertness and low porosity. Organic coatings consist of binders, pigments, solvent, adhesives and other additives and can be applied through physical methods or by electrostatics [11]. The binder is the main component.
- **Metallic Coatings:** Metallic coatings are layers of films created by the deposition of metal particles to the surface of other metals or other accepting materials. This is commonly applied in cases where the substrate metal is coated with a less reactive metal (noble metals such as gold), and the high efficiency of coating is only achieved in a non-porous and intact coating. A second variation involves the coating of the substrate metal with a more reactive metal, such as the coating of steel with zinc. This latter variant is effective when the product of the coating process is able to increase the electrochemical reactivity, i.e. corrosion [12]. Conventionally, metallic coating is approached through various methods such as: Electroplating, electroless coating, spraying, hot dipping, galvanizing, anodizing and organic Coatings.

Metallic coating techniques are used majorly to improve performance and give substantial corrosion resistance, while enhancing the visual perception of the material: Luster and reflection. Important materials used for metallic coating include, zinc, tin, nickel, gold, chromium, aluminum, cadmium and copper. Electroless coating comes in through as a metallic coating technique, where it is known as a chemical process that involves an autocatalytic response of the constituents in an aqueous mixture, involving multiple simultaneous reactions, with non-galvanic excitation, that causes the formation of thin film layers i.e. the coating, on the substrate of the material [13]. The reduction of metallic ions required to coat the surface of the metal occurs due to a reducing agent in that same compound, which supplies an intrinsic potential difference to allow current flow. This follows by the need for the cations of the deposition metal to be reduced by electrons receiving them at the substrate, electrons which the reductant also donates to this surface thereby undergoing oxidation [14].

3 Electroless Coating

Electroless coating technique, being a result of the cataclysmic event of the chemical reaction between the substrate and the bath components, gives an almost uniform thickness all over the substrate, with exceptional corrosion resistance and high hardness, all without the need to induce a current [13]. This enables the method to find sanctity in various areas of use where setting up a means of passing the electric current is unavailable. Electroless coating has become synonymous with Ni-P nickel coating as most coatings are done using the mix of nickel and phosphorus - the coating has become popular in its use for coating non-metals and had its biggest commercial success in printed wiring boards (PWBs), as miniature holes and various corners on the circuit board could now be coated directly. This most generally used electroless plating technique: the electroless nickel plating method, involves the deposition of uncrystallized nickel alloy on the substrate, with even thickness regardless of the shape and form of the material due to its independence on current.

Electroless coatings are reviewed to possess high tribo-corrosion resistances, enhanced mechanical properties and conductivity. Electroless coatings can further be subdivided into alloy coatings, metallic coating and composite coatings. Electroless metallic coatings involve the coating of materials with metals, while electroless alloy plating involves coating of alloys such as the alloy of nickel and phosphorus on the substrate. Composite coatings involve the co-deposition of particulate matter with an electroless compound, this type of coating dates back to as far as the 1960's, where Oderkerken Jules Marie, 1966, in his pursuit of the enhanced corrosion resistance of electrodeposited nickel deposited layers containing Al_2O_3 and PVC

particulates. A modern example of co-deposition would be the use of zirconium diboride which is categorized as a ultra-high temperature ceramic (UHTC) material, which due to its high temperature strength is used in high temperature applications [15].

ZrB₂ parts are usually sintered and hot pressed. It is also termed as unusual for displaying relatively high electrical and thermal conductivities. [16] studied the coating of graphite materials with ZrB₂-SiC and SiC, in a means to alleviate the poor oxidation reaction resistance of the engineering material. ZrB₂ was stated to possess properties such as high melting point, strength, temperature stability and good oxidation resistance, which could mean increased effectiveness in corrosion situations. Microstructure analysis and characterization was done using a scanning electron microscope and x-ray diffractometer, and results showed that the inclusion of the ZrB₂ particles gave definitive improvements to the samples ability to sustain various shocking cycles at high temperatures.

Various efforts have been put towards the reinforcement of materials using electroless nickel plating, with the most important reinforcement particles being refractory particles, such as: oxides, ceramics, precious stones, powders and carbides [17]. The magic of electroless coating occurs mainly in the baths. A typical nickel bath usually consists of: A nickel cation source, hypophosphite anions, an organic chelating agent, exaltant, stabilizers, pH regulators and wetting agents. Bath types are generally categorized into alkaline type baths or acidic baths, which can be further categorized into sulphamatic baths, fluoroborate baths, chloride/chloride-sulphate baths and watt baths [13].

By [13], stated in his work that the overall versatility, and increasing interest of the processes of electroless coating is attributed to the various advantages the process offers. The deposits of the electroless coating are more difficult to remove relative to conventional techniques of nickel coating due to the strong chemical bonding, giving it strong corrosion resistance. The deposits of electroless nickel coating possess good wettability and usually high hardness, but obtaining these characteristics from the bath is more difficult due to the complex nature of the bath preparation and maintenance. The bath also falls short in efficiency and can operate on higher costs than electrodeposition due to the heating of the bath contents and gradual evaporation of its constituents. Although, with the electroless coating system consisting only of the bath and heating element, with little additional equipment compared to electroplating, and no electricity required, this gives versatility of use with materials, such as non-conductors and benefits of large economical savings such as time, money and space. The electroless coatings also provide variable thicknesses all of uniformity on the substrate, regardless of shape or size allowing various kinds of corrosion to be averted, filling holes in the substrate.

[18] studied electroless plating on plastics and inferred electroless coating as a viable process for the coating of plastic materials with metals. This enables non-metals to be associated to metals through the sharing of various important metal characteristics such as: luster, reflectivity, resistance to abrasion, electrical conductivity and various other aesthetic properties. Other methods of metallization of plastics exist, many of which include electroplating, spraying and electroforming, but electroless plating is the most widely used method as the chemical reaction occurs autocatalytically without the use of any external electric power supply. The use of this method provides an electrically conductive surface on the non-conductive material, thereby allowing for conduction and further plating by electroplating, and thereby providing a better bonding. This makes up for the natural inability for the electroplating method, a more common alternative which can only work on metal, or “metallized” materials.

Future developments expected for electroless nickel and copper coating techniques include the shielding against electromagnetic radiation through coating with various ceramics such as glass, and evolution of tribo-corrosion resistive properties with increased impact against the school of thought today. Progressively reduced prices of electroless coatings and more versatility of use in the coating field [19].

3.1 Mechanisms of electroless coating

The autocatalytic chemical deposition of a metal such as nickel from an electrolyte filled with the salt of the nickel element is an electrochemical process that emulates the transfer of electrons between the reacting compounds as a result of the inherent redox reactions. Where the redox reaction stands for reduction-

oxidation reactions, reduction is characterized by the gain of electrons while oxidation is the opposite. For the reaction to be sustainable, there can be no depletion of the substrate material, while the nickel must be able to deposit on the initial substrate, and consequently on the newly developed layers iteratively [20]. This continuous deposition is achieved by the catalytic action of the deposit itself, hence the reason it is called an autocatalytic reaction. In general, a surface reaction such as the electroless nickel deposition can be categorized into the following basic steps:

- Reactant dispersion (H_2PO_2^- and Ni^{2+}) to the substrate;
- Reactant absorption at the substrate;
- Chemical reaction at the substrate;
- Rejection of products of reaction (HPO_3^{2-} , H^+ and H_2);
- Dispersal of products from substrate [20].

There are various theories on the actual mechanism of the electroless coating technique as the mechanism of the catalytic reaction is not well understood. Various mechanisms have been proposed towards the evolution of hydrogen in the reaction, theories which include the atomic hydrogen mechanism endorsed by Brenner and Riddell the creators of the electroless coating technique [21]; the hydride transfer mechanism advanced by Hersch; the pure electrochemical mechanism also proposed initially by Brenner and Riddell; and the metal hydroxide mechanism [22]. These mechanisms can account for most of the characteristics of the electroless coating technique, but cannot give an encompassing definition of the entire process. The characteristics of the electroless nickel coating that the mechanisms proposed fail to fully define are:

- Evolution of hydrogen always accompanies the reduction of nickel;
- The reduction reaction occurs at the substrate of specific materials known to be good hydrogenation-dehydrogenation catalysts, and also on the metal used for deposition;
- The deposit is made up of nickel and phosphorous/boron/nitrogen, dependent on the reducing element used;
- The molecular ratio of nickel deposited on the substrate to that of the reducing element used is less than or equal to unity;
- Hydrogen ions are products of the reducing reaction [22].

Even with the lack of thorough information on the mechanism of electroless coating chemistry, the possibility of a uniform mechanism that can be defined is still very much high due to the familiar nature of the process when compared in various situations [23].

3.2 Electroless coating setup

The electroless setup is similar to the more popular general electroplating setup, the only difference being that it is an autocatalytic reaction that is not galvanic: It does not require any external power source, or form of external electric excitation. The equipment for this technique includes a heater and stirrer, the electrolyte, an inert container and a thermometer to monitor the process. The samples which require coating will be immersed in a formulated bath properly developed to deposit the required coating material, heated to a certain working temperature, which activates the process. The bath composition is stirred at interval to allow effective dispersion of particles on the substrate. The Figure 1 shows a typical electroless coating setup.

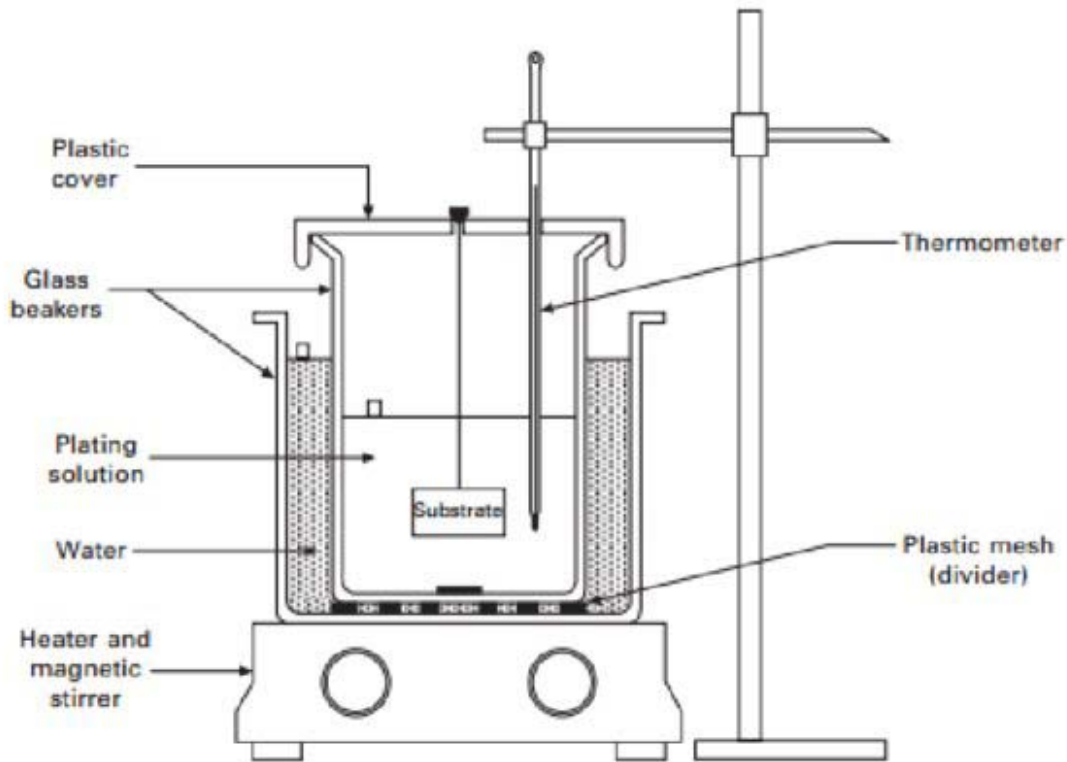


Figure 1: Electroless Coating Setup [24].

4 Industrial Applications of Electroless Nickel Coating

[25], stated in the study of corrosion of printed circuit boards in automobiles that the variable surface finishes on the automobile printed circuit is of utmost importance, as the aim of the coatings is to mitigate corrosion from gases in the average automobile working environment. The study involved the deposition of electroless nickel immersion gold (ENIG), electroless cobalt and immersion tin. The study concluded with electroless cobalt and nickel immersion outperforming immersion tin, with electroless cobalt showing only slight corrosion at 1500 ppm SO_2 , with no copper diffusion to the surface. The electroless method provides room for more technological advancement using the properties of plastics and metals as it is of use in various industries such as the aerospace, automobile and manufacturing industries [18].

Nickel.

From [26], the applications of electroless nickel in various industries such as that of the chemical process industry, food industry, oil and gas industry, automotive industry, aerospace industry and electronics industry is outlined. It is described in the chemical process industry as a means of reducing storage and maintenance costs, manufacturing and transportation costs as electroless nickel possesses excellent corrosion resistance and an immunity to stress corrosion cracking, implementation of this coating technology to their material handling equipment provides better efficiency and protection. In the food industry, electroless coating has many uses, although no coating technique yet has approval by the food and drug administration (FDA). Stainless steel is of a manifold of uses in the food industries as it is tested and trusted, but in cases where stainless steel cannot be used, manufactures utilize other lower grade stainless steels, aluminum alloys and carbon steel. In these cases, it is compulsory to coat these materials to make up for the material's lacking corrosion resistance. Electroless nickel coating is widely accepted and succeeded in coating various materials that do not make direct contact with the food. The oil and gas industry is known for its application of concurrent engineering practices and techniques to achieve the best possible safety and production methods, which showed itself as a practical and proper proving ground for electroless nickel.

This industry alone is reported to account for 15% of electroless nickel coatings in all of America. Various equipment is exposed to varying harmful environments in this case and the uniform corrosion resistant nature of electroless nickel coatings has been able to play a part in protecting various equipment: They are especially used in valves and flow control equipment.

In research, [27] studied electroless Ni-P composite coatings and the development of the coating is outlined, as well as the process of imbibement with particles and their over arcing effect on the mechanical, corrosion and physical properties of the coatings. It was detailed that the electroless nickel phosphorous alloy coating have better corrosion resistance than their composite counterparts with low attention given to their high temperature behavior, they tend to behave positively with larger oxidation resistances with the incorporation of particles such as Si_3N_4 , CeO_2 and TiO_2 in different gravimetric percentages. It was also given that electroless nickel phosphorous composite coating with B_4C reinforcement produces a material with a strong susceptibility to magnetic interference through magnetic fields when compared to the plain composite coating of nickel and phosphorous alone, however, on crystallization, they become homogenous and attain ferromagnetism.

5 Conclusion

The electroless coating technique is an exceptional coating technique that provides uniform film, optimum corrosion resistance and good hardness properties. The deposits of electroless nickel coating possess good wettability and usually high hardness but the process to obtaining proper results can be difficult. Therefore, comparing electroless coating to other more notable coating techniques such as electrodeposition, it can be inferred that the quality of the electroless coating is greater albeit the technique has weaknesses in its economic viability and rate of deposition, making it less of a choice for large scale industrial challenges and the preferred method for precision processes.

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