

Electroless Nickel Plating

Subjects: Others

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Electroless nickel (EN) plating is an auto-catalytic reaction that deposits an even layer of nickel-phosphorus or nickel-boron alloy on the surface of a solid material, or substrate, like metal or plastic. The process involves dipping the substrate in a bath of plating solution, where a reducing agent, like hydrated sodium hypophosphite ($\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$), reacts with the material's ions to deposit the nickel alloy. The metallurgical properties of the alloy depend on the percentage of phosphorus, which can range from 2–5% (low phosphorus) to 11–14% (high phosphorus). Unlike electroplating, it is not necessary to pass an electric current through the plating solution to form a deposit. Electroless plating prevents corrosion and wear, and can be used to manufacture composite coatings by suspending powder in the bath.[1] EN plating creates an even layer regardless of the geometry of the surface – in contrast to electroplating which suffers from flux-density issues as an electric field will vary due to the surface profile and result in uneven depositions. Depending on the catalyst, EN plating can be applied to non-conductive surfaces.

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1. Historical Overview

The EN plating of metallic nickel from aqueous solution in the presence of hypophosphite was a chemical accident by Charles Adolphe Wurtz in 1844.^[1] In 1911, Francois Auguste Roux reported that metal was inevitably precipitated in its powder form; however, this was not used in practical applications.^[2] In its early stage, progress in the field remained slow until World War II. In 1946, Abner Brenner and Grace E. Riddell developed a process for plating the inner walls of tubes with nickel-tungsten alloy, derived from the citrate-based bath using an insoluble anode, which brought out the unusual reducing properties of hypophosphite.^[3] The U.S. Patent Office says that the patent it issued in 1950 differed from the earlier patent in that the Roux reaction was spontaneous and complete, while the Brenner and Riddell process was a controlled catalytic process so that deposition occurred only on catalytic surfaces immersed in the bath.^[4] Brenner later wrote that his patent was an accidental discovery similar that of Wurtz and Roux, and filed a patent to protect the rights of the United States government. A declassified US Army technical report in 1963 credits the discovery to Wurtz and Roux more than Brenner and Riddell. EN plating was attributed to the chemical reduction of nickel ions.

During 1954–1959, Gutzeit at General American Transportation Corporation (GATC) developed electroless plating by chemical reduction alone, as an alternative to electroplating.^[5] Initially, the co-deposition of particles was carried out for electrodepositing nickel-chromium by Odekerken in 1966. In that study, in an intermediate layer, finely powdered particles, like aluminum oxide and polyvinyl chloride (PVC) resin, were distributed within a metallic matrix. One layer in the coating was a composite, but other parts of the coating were not. The first commercial application of their work was electroless nickel-silicon carbide coatings on the Wankel internal combustion engine, and another commercial composite in 1981 incorporated polytetrafluoroethylene (nickel-phosphorus PTFE). However, the co-deposition of diamond and PTFE particles was more difficult than that of composites incorporating aluminum oxide (Al_2O_3) or silicon carbide (SiC). The feasibility to incorporate the second phase of fine particles, the size of a nanometer to micrometer, within a metal-alloy matrix has initiated a new generation of composite coatings.^[6]

2. Process

Before plating, the surface of the material is cleaned by applying a series of chemicals. Unwanted solids left on the surface cause poor plating. After applying each pretreatment chemical, the surface is rinsed two to three times with water to completely remove the chemicals. Removing oils is known as *de-greasing*, and removing scaling is known as *acid cleaning*.

The pretreatment required for the deposition of nickel and cobalt on a non-conductive surface usually consists of making the substrate hydrophilic, then activating the surface with a solution of a noble metal, like palladium chloride. Silver nitrate is used for activating ABS and other plastics. The composition of the electroless bath depends on the activator.

Activation is done with a weak acid etch, nickel strike, or a proprietary solution, if the substrate is non-metallic. After plating, an anti-oxidation or anti-tarnish chemical, such as trisodium phosphate or chromate, is applied, followed by rinsing with water to prevent staining. The plated object is completely dried or baked to obtain the full hardness of the plating.

3. Characteristics

EN plating does not require electrical power, sophisticated jigs, or racks. The chemical replenishment is costly but can be monitored automatically, and complex filtration is not required. The lifespan of the chemicals, however, is limited. EN plating deposits an even coating of a desired thickness and volume, even in recesses and blind holes. The plating can have a matte, semi-bright, or bright finish. Because EN plating is porous, the quality of the material structure is inferior compared to electrolytic processes.

The specific characteristics vary depending on the type of EN plating and nickel alloy used, which are chosen to suit the application.^[7]

4. Types

4.1. Low-Phosphorus Electroless Nickel

Low-phosphorus treatment is applied for deposits with hardness up to 60 on the Rockwell C scale. It offers a uniform thickness on inner and outer surfaces of complex shapes, which often eliminates the need for grinding after plating. It is also excellent for corrosion resistance in alkaline environments.

4.2. Medium-Phosphorus Electroless Nickel

Medium-phosphorus electroless nickel (MPEN) has a phosphorus content of 4-10%, depending on its application. For decorative applications, 4–7% is considered medium-phosphorus; for industrial applications, 6–9%; and for electronics, 4–10%. The EN plating solution typically has eight components: nickel, a reducing agent, a complexing agent, stabilizers, buffers, brighteners, surfactants, and accelerators. Nickel sulfate is a typical nickel source, and sodium hypophosphite is a typical reducing agent. The complexing agent is necessary to increase phosphate solubility and to prevent the white-out phenomena by slowing the reaction. They are not co-deposited into the resulting alloy. Carboxylic acids or amines are typical complexing agents. Stabilizers, like lead, sulfur, or organic compounds, slow the reduction by co-deposition with the nickel. Most complexing agents act as buffers. Brighteners are mostly co-deposited with nickel, and usually are stabilizers, like cadmium or certain organic compounds. Surfactants lower the surface tension to reduce pitting and staining. Accelerators such as sulfur compounds are added to overcome the slow plating rate caused by complexing agents and usually are co-deposited, often discoloring the deposit.

MPEN plating deposits quickly and is very stable, with bright and semi-bright finishes. The processing often used for equipment in slurry disposal industries.^[clarification needed] This is the most common type of electroless nickel applied.

4.3. High-Phosphorus Electroless Nickel

High-phosphorus electroless nickel offers high corrosion resistance, making it ideal for industry standards requiring protection from highly corrosive acidic environments such as oil drilling and coal mining. With microhardness ranging up to 600 HV, this type ensures very little surface porosity where pit-free plating is required and is not prone to staining. Deposits are non-magnetic when phosphorus content is greater than 11.2%.^[8]

5. Applications

The most common form of electroless nickel plating produces a nickel-phosphorus alloy coating. The phosphorus content can range from 2% to 13%. Such plating is used when wear resistance, hardness and corrosion protection are required. Applications include oilfield valves, rotors, drive shafts, paper handling equipment, fuel rails, optical surfaces for diamond turning, door knobs, kitchen utensils, bathroom fixtures, electrical/mechanical tools and office equipment. It is also commonly used as a coating in electronics printed circuit board manufacturing, typically with an overlay of gold to prevent corrosion. This process is known as electroless nickel immersion gold.

Due to the high hardness of the coating, it can be used to salvage worn parts. Coatings of 25 to 100 micrometers can be applied and machined back to the final dimensions. Its uniform deposition profile means it can be applied to complex components not readily suited to other hard-wearing coatings like hard chromium.

It is also used extensively in the manufacture of hard disk drives, as a way of providing an atomically smooth coating to the aluminium disks, the magnetic layers are then deposited on top of this film, usually by sputtering and finishing with protective carbon and lubrication layers; these final two layers protect the underlying magnetic layer (media layer) from damage should the read / write head lose its cushion of air and contact the surface.

Its use in the automotive industry for wear resistance has increased significantly. However, it is important to recognize that only End of Life Vehicles Directive or RoHS compliant process types (free from heavy metal stabilizers) may be used for these applications.

6. Standards

- AMS-2404
- AMS-C-26074
- ASTM B-733
- ASTM-B-656 (inactive)^[9]
- MIL-DTL-32119

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