

## LOW TEMPERATURE AUTOCATALYTIC NICKEL DEPOSITION

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Autocatalytic nickel deposition was first patented in 1955. This work was carried out to develop an autocatalytic nickel deposition process at lower temperatures. This process was based on same electrolytes and reducing agents viz; hypophosphite but it worked at lower temperature and contained sodium fluoride. Plating rate was good and the deposits contained less phosphorous content. It was also observed that the deposits have good adhesion and was comparable with electrodeposited nickel in corrosion resistance and relatively easy in the practical application of deposition.

**Key words:** Low temperature, Nickel plating, Autocatalytic, Nickel deposition, Reducing agents, Hypophosphite.

### Introduction

Autocatalytic nickel deposition was widely used for the protection of metals against corrosion damage. Most of the autocatalytic process involved working at high temperature of 90-95°C. Brenner and Riddell in their work found that acid plating solutions were advantageous as compared to alkaline solution due to high speed of separation, greater stability, easy control of solution and better properties of nickel-phosphorous coating. They also found no significant influence of the concentration of hypophosphite on the speed of separation of glycolate solutions with a similar solution. However, solution contained less glycolic acid (Brenner and Riddell 1947). The concentration of nickel ions was 5-10 g/l and has been separated in the organic solutions. Gutzeit described that nickel-cobalt (only in alkaline solutions) Rhodium and Palladium can be directly non-electrolytically plated. High alloy steel, cast iron, brass, bronze and aluminium, magnesium alloys can be autocatalytically nickel plated. After proper pretreatment plastics, glass, ceramics and semi-conductors can also be autocatalytically nickel-plated (Gutzeit and Kanigen 1954). Lukes suggested that the interaction between the hypophosphite ion and the water leads to the formation of hydride ion  $H^-$  which appears as a reducing medium of the nickel ion ( $Ni^{2+}$ ). The hydride ion did not become a proton but it was only oxidised to atomic hydrogen and the latter forms molecule was given off as hydrogen gas (Lukes 1964). Wiegand suggested that for most acid solutions for autocatalytic nickel coating surface to volume S/V lies between 1.5-3  $dm^2/l$  (Wiegand and Kaiser 1965). Other reducing agents used i.e. alkali boron-hydrides and their derivatives and certain boron-nitrogen compounds as reducing media, they exhibited a higher reducing activity as com-

pared to hypophosphite ions and some of them were used for coating at low temperatures thus suitable for coating on thermally unstable materials. Saubestre was the major contributor in the field of autocatalytic nickel deposition process (Saubestre 1967). Temperature was the most important factor governing the speed of the process. The reducing reaction needs energy provided in the form of heat (Ouyang *et al* 2000). Lee had studied the low temperature lytic deposition process (Lee 1960a). Autocatalytic deposition process has reported that working took places at 21°C and the rate to deposition was very low as it is 1  $\mu m/h$  (Lee 1960b). This work involved the study of autocatalytic deposition process at lower temperature but with increased rate of separation.

The chemicals used for this study were of reagent grade. The composition of the bath used is as follows:

Nickel chloride with  $6H_2O$ , 12-15 g/l; sodium hypophosphite, 17-12 g/l; boric acid, 15-18 g/l; sodium fluoride, 5-7 g/l and pH was 6.

The pH of the solution was adjusted to 6 with HCl. Mild steel panels after degreasing in an emulsion cleaner for 30 min at 80-90°C were subjected to hot rinsing for 2 min. at 40°C, then pickled in HCl 20% by volume for 1-2 min, followed by cold rinsing and immersed into the autocatalytic depositing solutions for different intervals of time at a temperature of 65°C and then at 70°C.

**Thickness measurements.** Cross section were cut from deposited panels, mounted and polished to 1  $\mu m$  finish with diamond pastes after grinding to remove any scratch. The thickness of the deposited layer was measured under the

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optical microscope. Deposited layers were stripped from the panels and analyzed for the phosphorous contents.

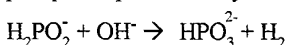
### Results and Discussion

The results obtained from the autocatalytic deposition of nickel plating are shown in Tables 1-3.

*Salt spray test.* The steel panels deposited with autocatalytic nickel deposits containing 5.6% phosphorus contents were compared for their protective behaviour with electro deposited nickel by subjecting them to Corrosion Accelerated Salt Spray Test (Lee 1960a) in Table 3.

In Table 1, the temperature plays very important role in the autocatalytic deposition speed of nickel for different durations varying from 30-60 min. During the course of experiment, heating of the separating solution was avoided because the process of the dissociation of the reducing medium may take place quickly. Hypophosphite ion was oxidised to orthophosphite ion in the presence of catalytic surfaces, hydrogen gas evolving during this reaction was partially absorbed on the surface of the substrate. The nickel ions were reduced to metallic nickel by active hydrogen atoms where by they oxidised to hydrogen ions. At the same time a small part of the hypophosphite ions reduced to OH<sup>-</sup> ions, water and phosphorus by the adsorbed active hydrogen on the catalytically acting surface. The speed of the reaction was inverted function of pH value. A part of the hypophosphite ions was oxidised catalytically to orthophosphite ions, whereby gaseous, molecular hydrogen gas was given off. The latter reaction takes place independently of the separation of nickel thus the output was about 38% (Brenner and Riddell 1947).

From Table 2, it was cleared that the content of phosphorous decreased at higher temperature in acid solution was suggested by Baldwin and Such (1966). The pH of the solution was maintained to 6. However, the rate of deposition increases with the increase in pH but the minimum value of pH where any deposition was observed is 3. At neutral pH i.e., 7 hypophosphite spontaneously oxidises as



Optimum pH value was above 5 and below 7 because for the pH values ranging between 4.3-4.9 bath exhibit poor physical properties (Brenner and Riddell 1947; Gutzeit and Kanigen 1954; Gutzeit 1954; Metheny and Lee 1956; de Minjer and Brenner 1957; Cahill 1957).

Autocatalytically nickel plating shortens the production process as bright nickel can be easily deposited on the nickel layer and as described earlier solution for autocatalytic nickel plating were more stable. Also it allowed greater degree automation of the process for plating on to plastics and polymer.

**Table 1**  
Autocatalytic deposition of nickel plating

No. of experiment	Time (min)	Temperature °C	Thickness of deposited layer μm
1	30	65	8
2	60	65	16
3	30	70	9
4	60	70	18

**Table 2**  
Autocatalytic deposition of nickel containing phosphorous

No. of experiment	Time (min)	Temperature °C	Phosphorous contents %
1	30	65	5.4
2	60	65	5.6
3	30	70	5.0
4	60	70	5.1

**Table 3**  
Electrodeposition of nickel by corrosion accelerated salt spray test

Nature of the deposit	Area corroded	Corrosion rating
Electro deposited nickel	0.002%	8
Autocatalytic nickel	0.003%	7

### Conclusion

The corrosion behaviour of the autocatalytic nickel deposited at lower temperature was comparable with the electrodeposited nickel having corrosion rating of 7. It was possible to obtained autocatalytic nickel deposits at low temperature with reasonable rate of deposition having low phosphorus contents. This type of deposits can be easily used for deposition on polymers and plastics particularly for PCB without any physical damage as it works at low temperature.

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