

Study of stabilisers as special additives to Acid Hypophosphite solutions for Electroless Nickel plating

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Abstract: In any bath for electroplating, additives serve to increase speed of reaction, to increase reliability and also to protect the base metal. Properties such as lustre, porosity, internal stresses are markedly altered. I investigated certain additives with respect to the speed and lustre of the coatings. These additives are sodium thiosulphate and potassium ferrocyanide containing sulphide and cyanide ion respectively. These ions are known to inhibit and retard the reaction. Experimentally, we proved that when these are used in certain concentrations, they serve to stabilise the bath and prevent immature its decomposition. Life span of a bath is a very important parameter in Commercial set-up. However the concentration levels of these additives are crucial for bath longevity. A slight excess can totally stop the reaction and in some case slightly lesser amount can have the opposite effect of accelerating the reaction. The concentration required may also vary with the Ni^{+2} /hypophosphite ratio and the type of complexing agents used in the reaction. Sodium thiosulphate and Potassium ferrocyanide did not give any improved lustre of the coatings.

Keywords: Electroless Nickel, stabilisers, Acid Hypophosphite, accelerators.

Introduction:

Non-electrolytic deposition of metals particularly that of Ni always occurs as Phosphorus or Boron alloy. It was invented by A. Brenner and G. Riddell in 1946¹. This process which takes place without the use of electricity permits deposition of metal from its salt solution on catalytically active surfaces such as mild steel. Nickel Chloride and Nickel sulphates as source of Nickel are commonly used. The reducing

medium most commonly used is Acid Hypophosphite²⁵. An alkaline hypophosphite medium gives porous Ni coatings with lower Phosphorus content. An alkaline hypophosphite medium also yields lustrous coatings with need for fewer additives. Recent efforts are directed towards substitution of ammonia with amines such as EDTE, ethylene diamine, triethanol amine and diethanol amine. In order to avoid ammonia, acid hypophosphite bath with substrates of mild steel which are catalytically active are used.. Ni, Co, Pd, Rh are truly catalytically active³²². That means that they do not need any special activation. The more noble elements than Ni such as Cu, Ag, Au Cr and Carbon can be activated by short cathodic impulse. Mild steel substrates do not need to be activated but they need to be pickled and cleaned before use.

In any process for plating metals, the speed is the most important factor, the next being the influence of temperature⁴²⁸ and pH⁵³². The temperature of 90C – 98C is required for Acid hypophosphite bath. As reaction proceeds the concentration of H^+ ions increases with reduction of Ni^{+2} ions and pH decreases. Usually decrease of pH leads to coatings with greater Phosphorus content. Maintaining pH becomes important for uniform coatings with desired Phosphorus content. For this reason buffer forms an important additive in Electroless baths. I have used citric acid as the most common buffering agent. Another important class of additives are stabilizers. The role of stabilizers is to prevent

spontaneous and premature decomposition of the bath.

Experimental:

It is desirable to have optimum concentration of hypophosphite in the range of 0.15-0.35 moles/l. The optimum mole ratio of $\text{Ni}^{2+}/\text{H}_2\text{PO}_2^-$ should be in the range 0.3-0.457⁷²⁸. The composition for all the three baths was as follows:

Bath 1 (Control Bath without any stabilizer)

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O} = 24.64 \text{ g/l}$
Sodium Hypophosphite = 26.4g/l
Organic acid (Succinic acid) = 2.7/l
Sodium citrate = 10g/l

Bath 2 (employing Potassium ferrocyanide as stabilizer)

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O} = 24.64 \text{ g/l}$
Sodium Hypophosphite = 26.4g/l
Organic acid (Succinic acid) = 2.7/l
Sodium citrate = 10g/l
Potassium Ferrocyanide = 20mg

Bath 3 (employing Sodium thiosulphate as stabilizer)

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O} = 24.64 \text{ g/l}$
Sodium Hypophosphite = 26.4g/l
Organic acid (Succinic acid) = 2.7/l
Sodium citrate = 10g/l

Sodium Thiosulphate = 500mg

Procedure followed with all the three baths involved maintaining the following conditions during the reaction time:

pH = 4.5 (Ammonia was used to adjust the pH)

Temperature = 85-90

Time of deposition = ½ hour

Stirring = occasional

Prior to deposition the substrate which was mild steel was cleaned and suitably etched. The substrate dimensions were 5.0 cm by 1.0 cm with thickness of 1.0mm. The rate of deposition was measured by weighing the M. S. strip before and

after the deposition. 80 ml of the bath was used. The pH was adjusted with Ammonia. The reaction time was maintained for half an hour after which the substrate was removed from the bath. The substrate was washed, cleaned with Distilled water and dried in a dessicator after which it was weighed. The procedure was carried out on Day 1, Day2 and Day 3.

Results and Discussion:

The amount of Ni deposited with each bath on different days was tabulated as under

	Day 1	Day 2	Day 3
Bath 1	22.0 mg	11.0 mg	5.2 mg
Bath 2	21.7 mg	15.7 mg	10.3 mg
Bath 3	22.5 mg	15.8 mg	10.1 mg

The data shows that the amount of Ni deposited decreases from Day 1 to Day 3 for all the baths. On Day 1 when the baths are freshly made, the rate of deposition is almost similar. However the subsequent decrease in deposition is less for Bath 2 and Bath 3. Also it was observed that Bath 1 decomposed in a week's time while Bath 2 and Bath 3 were unaltered. These results are summarised in Table 2:

Bath 1	Control Bath	Decomposed
Bath 2	Employing potassium ferrocyanide	Unaltered
Bath 3	Employing sodium thiosulphate	Unaltered

The results indicate that sulphide and cyanide ions in Bath 3 and Bath 2 act as stabilisers and serve to lengthen the life of the Bath. Without decomposition the Bath decomposes prematurely. The life of Bath in a commercial set up is important for maximum output. At the same time the stabilisers used need to be

compatible with the existing components of the bath. The amount of stabilisers usually need are of the order of few milligrams. It is possible that when used in even lower concentrations, they serve to speed up the reaction. Another factor with regard to quality of coatings is their lustre. Lustre may or may not improve with addition of stabilisers. It was observed in this set of experiments that there was no improvement in lustre. All the baths yielded the same optical quality of Nickel coatings, namely with no lustre. In general we must increase the quantity of stabiliser if too much Nickel is precipitated on the walls of the bath container and we must reduce the concentration of stabilizer if discoloured coatings especially on sharp edges are obtained.⁸²⁶

Conclusion

Stabilizers form an integral part of any bath for depositing metal as they lengthen the bath life and make the process economically viable⁹⁶⁰. Without stabilizers the cost would significantly go up. Stabilizers need to be compatible with the bath components and they should be stable at the bath temperature and the pH at which the metal is deposited¹⁰⁶¹. It is worthwhile to investigate the fact that stabilizers in smaller amounts could act as accelerators. Stabilizers could then perform the dual function of stabilizing the bath life and acceleration the reaction to give shorter reaction times. Thiourea is a well known traditional stabilizer. Its use makes the coatings lustrous. However thiourea is needed to be added in ppm and it is difficult to control its concentration. A slight excess totally stops the reaction or gives porous coatings whereas in lesser amounts, the coatings that result are without lustre. A robust stabilizer is needed for deposition of lustrous coatings with stable bath life. A large class of stabilizers belong to the one containing cyanide and sulphide ions. In conclusion, the primary role of stabilizers is to

prolong the bath life by preventing premature decomposition of Ni salt from its solution. The secondary function of stabilizers is to increase the speed of separation of Ni coatings so that shorter reaction times result. The tertiary function is to add lustre to coatings. The challenge in most cases is to find the optimum concentration so as to give all the three benefits associated with a stabilizer.

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