Title: Role of Organic Acids in Electroless Nickel bath and their stabilization thereof

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Type of Project: Minor Research Project
Description of the project

The role of organic acids such as Succinic acid, Lactic acid and maleic acid in non-electrolytic (electroless) nickel baths were investigated with respect to their stability constants. The stability constants were determined with Bjerrum-Calvin method. They were found to decrease in the order Succinic acid > Lactic acid > Maleic acid. In this set of complexing agents the relationship between deposition rate and stability constant did not follow the reverse order as expected. It is possible that apart from the stability of the complexes, other factors such as buffering action and ability to stabilize the solution may play a part in the rate of deposition.

Electroless or non-electrolytic nickel plating which involves nickel plating without the use of electricity on an autocatalytic substrate such as mild steel was invented by A. Brenner and G. Riddell in 1946. Since then the process has been refined by new additives and varying conditions of deposition. There are some distinct advantages of electroless nickel over galvanic or electrolytic nickel plating. Galvanic nickel plating is difficult to apply to complicated shapes and is not sufficiently hard. It is limited to conventional metal components. Dielectrics and semiconductors cannot be nickel coated by galvanic means. Electroless nickel plating overcomes these limitations and even complements it by bridging the gap between the mechanical properties of galvanic nickel coatings and electroless nickel coatings.

The Electroless process can be represented as

\[ R^{n+} + R^{(n/z)+} + ze \]

\[ Me^{2+}ze \rightarrow Me \]

R is the reducing medium, namely, sodium hypophosphite. The substrate used was mild steel. Such substrates are autocatalytic to deposition of nickel by non-electrolytic method. The rate of deposition depends upon various factors such as temperature and pH of the bath ratio of concentration of nickel ions to hypophosphite, concentration of nickel, relationship of surface of the substrate to volume of the bath, nature and concentration of the complexing agent. The rate of the reaction also depends on nature and concentration of such additives such as accelerators, stabilizers and lustering agents. The function of the complexing agents such as organic acids is two-fold: Firstly, the organic acids act as buffer and prevent the pH value of solution from decreasing too fast. Secondly, they form nickel complexes thus reducing the concentration of free nickel ions and stabilizing the solution by preventing the precipitation of nickel phosphite.
In our study we chose three organic acids namely, 1) Lactic, 2) Succinic and 3) Maleic acid to investigate their role vis-a-vis their effect on speed of deposition. Lactic acid a hydroxyl carboxylic acid is a rare example of an organic additive which at the same time has the effect of complexing agent and a significant capacity for buffering action\(^4\). At optimum concentration it also has an accelerating effect. Succinic acid, a saturated non-substituted dicarboxylic acid is known for accelerating effect on the rate of deposition\(^5\). Maleic acid an unsaturated organic compound is also a known example of stabilizer\(^6\). Stabilizers are additives used for stabilization of the bath and to prevent its premature spontaneous decomposition of the electroless bath. The stability constant of Ni-organic acid complex was determined by Bjerrum-Calvin method. The rate of deposition was determined by simply weighing the substrate, which was mild steel, before and after the deposition process. We have to establish a correlation between the stability constants and rate of deposition.

Experimental work

AR grade nickel sulphate hexahydrate, sodium perchlorate, perchloric acid, succinic, lactic and maleic acids were used. All chemicals were used without purification. Distilled water was used for dilution purposes.

The experimental work consisted of two parts. In the first part the stability constants of Ni complexes was determined by Bjerrum-Calvin method.

The Bjerrum method: Following titrations were carried out:

1) 5cm\(^3\) of 0.2N HClO\(_4\) solution and 5 cm\(^3\) of 1 M NaClO\(_4\) solution is diluted up to 50 cm\(^3\). This solution is titrated against 0.2 N NaOH solution.

2) 5cm\(^3\) of 0.2N HClO\(_4\) solution and 5 cm\(^3\) of 1 M NaClO\(_4\) solution and 10cm\(^3\) of 0.01 N organic acid is diluted to 50 cm\(^3\) and titration is carried out against 0.2 N NaOH solution.

3) 5cm\(^3\) of 0.2N HClO\(_4\) solution and 5 cm\(^3\) of 1 M NaClO\(_4\) solution and 10cm\(^3\) of 0.01 N organic acid and 10cm\(^3\) of 0.01M Ni\(^{+2}\) solution is diluted up to 50 cm\(^3\) and titrated against 0.2 N NaOH solution.

From this data, pK\(_1\) and pK\(_2\) values are determined and eventually the stability constants K of the Ni-acid complex in form of log K are reported.

Electroless deposition: Deposition of Nickel on M.S. strip by non-electrolytic method was carried out by non-electrolytic method.
The Bath composition was as follows:

\[
\text{NiSO}_4\cdot 6\text{H}_2\text{O} = 0.09375 \text{ moles/l} \\
\text{Sodium Hypophosphite} = 0.25 \text{ moles/l} \\
\text{Organic acid} = 0.0468 \text{ moles/l} \\
\text{Sodium citrate} = 10\text{g/l}
\]

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 0.3-0.45. Sodium citrate has excellent buffering capacity.

Following were the conditions of deposition:

- \(\text{pH} = 4.5\) (Ammonia was used to adjust the pH)
- \(\text{Temperature} = 85-90^\circ\text{C}\)
- \(\text{Time of deposition} = \frac{1}{2}\) hour
- \(\text{Stirring} = \text{occasional}\)

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 1.0 mm. The rate of deposition was measured by weighing the M. S. strip before and after the deposition.

**Results and discussion**

<table>
<thead>
<tr>
<th>Organic acid</th>
<th>(\text{pK}_1)</th>
<th>(\text{pK}_2)</th>
<th>(\log K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic acid</td>
<td>(3.3204 \times 10^{-4})</td>
<td>(1.8050 \times 10^{-9})</td>
<td>3.52</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>(5.7756 \times 10^{-7})</td>
<td>-</td>
<td>3.14</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>(7.9432 \times 10^{-5})</td>
<td>-</td>
<td>2.52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic acid</th>
<th>(\log K)</th>
<th>Amount of Ni deposited in 0.5 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic acid</td>
<td>3.52</td>
<td>21.3 mg</td>
</tr>
</tbody>
</table>
Table 1 reveals that the second hydrogen of Lactic acid and maleic acid are not sufficiently hydrolyzed.

Table 2 shows the correlation of the stability constants with the deposition rate on M.S. steel.

The results show that the rate of deposition and stability constant follow an order except for succinic acid. Among the three acids studied the stability constant for succinic acid is highest. Succinic acid is known to have an accelerating effect on the rate of deposition. Indeed, among the three acids, succinic acid showed the highest rate of deposition.

With increasing stability constant the speed with which Ni is deposited is reduced. The log K values for Lactic is less than that for Maleic acid. The rate of deposition for lactic acid is greater than that for Maleic acid. One can assume that certain special influences also play a part which has no connection with the properties of the acid as a complexing agent. In our study, no stabilizing agents or lustering agents were added to keep the bath as simple as possible.

**Outcome of the project:** A paper was published as a result of the series of experiment carried out under this project, the details of which are as follows:

**Title of the paper:** Correlation between stability constants of Organic acids and their effect on rate of deposition in non-electrolytic nickel baths  
**Authors:** S.S Kokane, F. N. Ansari, R. P. Chavan and G. R. Bhagure  
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