

Electrodeposition of Nickel from Nickel Perchlorate Solution

F. C. MATHERS and BYRON W. NEHER, Indiana University

Wesley and Carey (Trans. Electrochem. Soc. 75, 209) studied the properties of a nickel chloride-boric acid bath. Their deposits were smooth and showed less tendency to tree than did those from the standard sulfate bath. However, the deposits were, in most cases, very dark and somewhat less ductile than those obtained from the sulfate solutions. Anode corrosion was very good. In fact, additions of hydrochloric acid had to be made to maintain the desired pH because the anode dissolved faster than the metal was plated out. The tank voltage was lower using the chloride solutions than in the sulfate bath, probably because of better anode solubility. The chloride deposits were finer grained than the sulfate, hence mechanical polishing was easier.

These authors claimed that the wide range of plating conditions under which sound deposits are obtained, the greater freedom from pitting, and the high anode and cathode efficiencies, all contribute to making this bath easier to operate and more nearly foolproof than the sulfate bath.

Experimental Work

In this investigation a study was made of nickel perchlorate-boric acid solutions for plating nickel on iron. Plates obtained from it were compared with those from the standard sulfate bath, and the nickel chloride bath as used by Wesley and Carey.

Composition of Solutions

Perchlorate bath. The composition was as follows: Nickel perchlorate 444 g./L. and boric acid 30 g./L. No nickel perchlorate was available; hence the solution was made from nickel carbonate and perchloric acid. The solution was heated to promote reaction. (When all the carbonate was dissolved, the solution was heated to promote reaction.) When all the carbonate was dissolved, the solution was diluted to one liter and filtered. A small amount of brown precipitate of unknown composition was always present. The filtrate gave no precipitate when tested with silver nitrate. Finally 30 grams of boric acid were added to the warm solution. The pH of the solution was adjusted as required by adding perchloric acid for lowering and nickel carbonate for raising the pH.

It was found necessary to "age" the bath before a satisfactory plate could be obtained. One liter of solution was run at a current density of 50 amp./sq. ft. for about 16 hours before a smooth plate was obtained. The reason for this is as yet undetermined, but perhaps it was due to small amounts of copper in the nickel carbonate.

Chloride and sulfate baths were made of the usual compositions.

No additions were made to any of the baths to prevent pitting or

to brighten the deposit. The solutions were not agitated except for stirring by hand at intervals during the operation.

Anodes

The anodes used for the chloride and sulfate baths were made of rolled nickel. Those for the perchlorate were slices sawed from a large cast nickel anode which contained considerable impurities. The cast anodes corroded very well in the perchlorate bath but the rolled nickel would not.

Apparatus

One hundred ml. of each solution were placed separately in three 150 ml. beakers using one anode to each solution. The cathode plates were pieces of "tin" cans which had been detinned with hydrochloric acid. They were 1½ inches square with a surface on one side of 2.25 sq. in. The cathodes were suspended by iron wires.

Plating Range

The three solutions were run in series at 25°C. and plates were obtained at different current densities and different pH's of 5, 4, 3, and 2. The current densities were 32, 51, 77, and 144 amp./sq. ft. A similar series was run at 60°C.

Anode bags were used on the sheet nickel anodes, but none was used on the cast nickel in the perchlorate bath. The cast nickel anode was scraped after each run to remove impurities from the surface and prevent polarization. Deposits were made 0.001 in. thick.

Deposits from the sulfate bath at 25°C. became slightly lighter in color as the current density was raised. The tendency to peel increased with increase in pH and also with increase in current. Nearly all of the deposits were ductile. Evidence of building up in thickness and treeing at the corners was noticed at pH 2 and 144 amp./sq. ft.

All deposits from the nickel chloride were dark in color except at pH 2 and 144 amp./sq. ft. which were light gray. All plates at pH 5 were unsatisfactory due to cracking over the entire surface. There was very little evidence of pitting. At high current densities, peeling or cracking decreased as pH was lowered.

All plates from nickel perchlorate (25°C.) were light colored and some had bright areas or streaks of brightness. Nearly all deposits were brittle and peeled somewhat at the corners. The plates obtained at a pH of 4 and a current density of 50 amp./sq. ft. were less brittle than under other conditions.

The anode corrosion was good except at high current densities. The pH's of the solutions remained fairly constant. The degree of change being not over 0.3 pH for about ½ amp. hr. except at high current densities. In the pH 4 solution the acidity stayed more nearly constant than in the other solutions. At pH 5 the acidity went up and at pH 2 and 3 the acidity went down slightly in most cases.

In the sulfate and chloride baths the pH increased in all solutions during runs, and the change was greater the lower the pH. The chloride bath showed greater efficiency of anode corrosion than any of the other baths. Deposits from all three solutions were smooth and practically free from pits.

Almost all plates from the sulfate were slightly pitted at 60°; this is in contrast to those obtained at the lower temperature. Also the deposits were darker in color at 60°. There was no peeling and the plates were ductile.

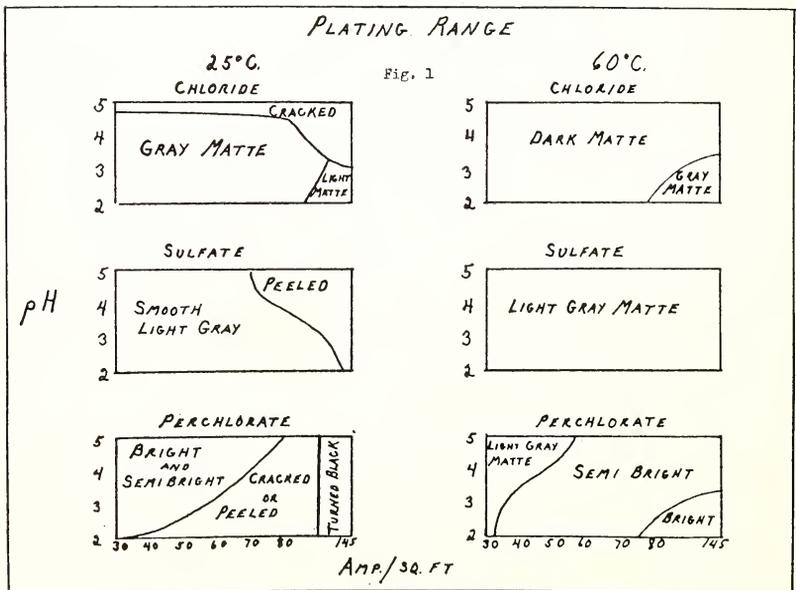
All plates from the chloride were very dark and smooth with very few pits. There was no cracking or peeling. The deposits became slightly lighter in color as the current density was raised and the pH lowered.

The perchlorate deposits at 60° were, for the most part, less bright than those at 25°; however, at the higher temperature there was no evidence of peeling or cracking and also the plates were more ductile. Higher temperatures permitted use of higher current densities. The brightness of the plates appeared to vary directly with the current density and inversely with the pH in the range tested.

The pH remained nearly constant, varying on the average only about 0.2 for each run. The pH generally became lower during the operation; at pH 2 however, it went up at the lower current densities.

The perchlorate bath gave lighter colored deposits than either the chloride or sulfate. The sulfate showed more pitting at 60° than the other two baths. At the higher temperature the ductility of all deposits appeared about the same, but at 25° the perchlorate gave the most brittle plates. There was very little hydrogen evolution in any of the solutions but a pH 2 gave the greatest amount. Higher current densities at a given pH showed less pitting.

The charts best show the general effects of variation of the current density and pH at 60° and 25° for the three baths as regards brightness or color (Fig. 1).



Ferricyanide Spot Test for Porosity

Ferricyanide gel tests were made with a warm solution containing 10 grams agar, 10 grams sodium chloride, and one gram of potassium ferricyanide per liter of solution. The warm solution was applied to the specimens while they were in a horizontal position and permitted to gel for 5 minutes. The total number of blue spots visible at a distance of about two feet was counted at the end of this time. Plates used were one and a half inches on a side. The desposits were 0.001 in. thick. Tests were made on plates obtained at 25° and 60°C.

Number of Spots

Plate No.	Perchlorate		Sulfate		Chloride	
	60°	25°	60°	25°	60°	25°
1	7	3	5	5	15	4
2	4	4	13	8	10	10
3	3	0	10	4	8	5
4	1	6	7	6	1	6
5	5	2	8	3	7	6
6	4	2	5	2	5	9
7	3	3	7	4	10	11
Average	4	3	8	5	8	8

The chloride and sulfate deposits have about equal covering power when run at 60°, but the sulfate gave a better plate at 25°. Deposits obtained from the perchlorate bath showed greater freedom from pores. However, as mentioned previously, the deposits made at 25° were brittle and some plates peeled. Probably polished cathodes as base metal would have given better results.

Cathode Efficiency

Cathode efficiency measurements in nickel baths are important in that they give an indication of the throwing power of the bath. If the cathode efficiencies were different from the anode efficiencies the pH of the baths would change proportionally as well as the composition of the bath.

The throwing power may be defined as that property of a solution by virtue of which relatively uniform distribution of metal is obtained upon cathodes of irregular shape. The current density at points of depression will obviously be lower than at raised points. Then if the current efficiency of the bath is low at low current densities, there will be very little metal deposited in these depressions. Therefore, in order for a plating solution to have good throwing power the current efficiencies at low current densities should be high. The rate of lowering of the current efficiency as the current density is lowered gives a measure of the throwing power of the bath. The best current efficiencies are shown in the curves (Fig. 2).

Thick Deposits

The chloride, sulfate, and perchlorate baths were run at 60° and a pH of 4 for about 17 hours at a current density of about 175 amp./sq.

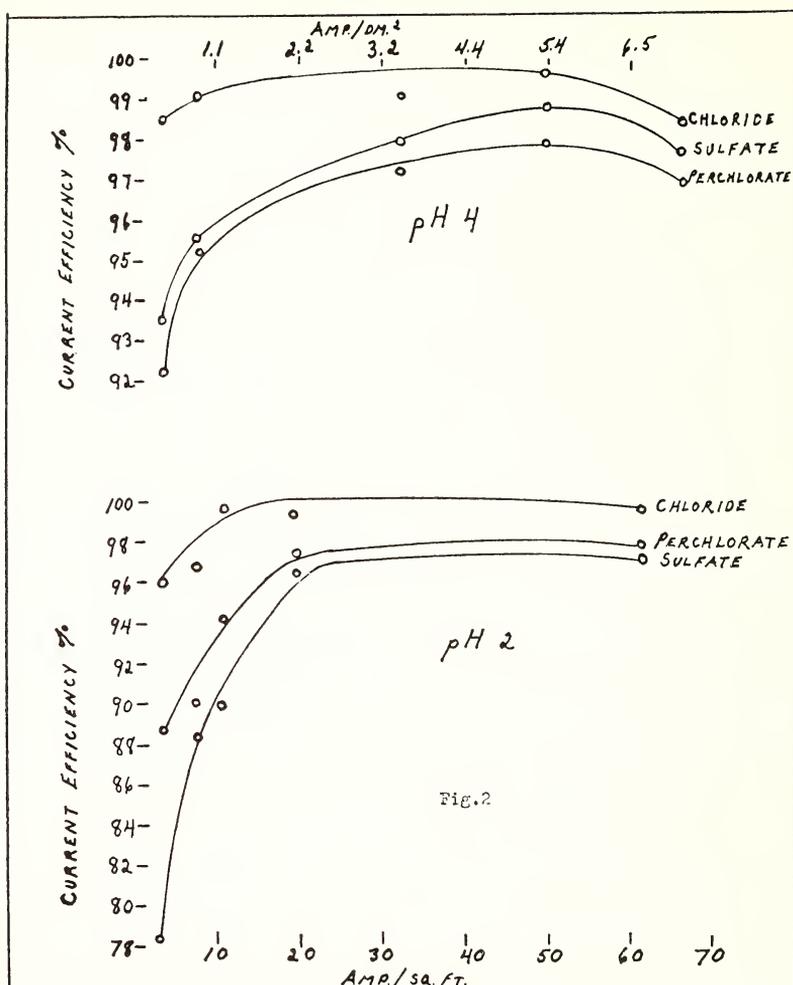


Fig. 2

ft. to determine the relative treeing and nodule formation tendency for each bath.

The ordinary sulfate baths showed a rather strong tendency to form trees and nodules on the corners of the plate; this effect increased as the current density was raised. Nodules formed on the surface of a plate are caused chiefly by the presence of suspended, conducting particles which adhered to the cathode. The surface of the sulfate plate was light gray in color and was covered with pits. The chloride and perchlorate solutions gave good plates free from nodules and trees. The chloride plate was dark gray and smooth; the perchlorate was bright and free from pits but the surface was somewhat rough. At the lower current density the sulfate showed less treeing, but large nodules were still formed at the corners. The surface of the plate was

light gray and covered with pits. The chloride plate obtained at the lower current density was the same as that at high current density. The perchlorate gave a smooth light colored plate, but was not bright. The pH of all solutions stayed about the same.

Summary

In comparing the nickel perchlorate bath with the sulfate and chloride baths it was found that the perchlorate gave brighter plates which were more free from pin-holes.

Very dark plates were obtained from the chloride solutions except at current densities between 80 and 144 amp./sq. ft. and pH 2 and 3.

The sulfate bath gave a light gray somewhat pitted plate under all conditions at 60°.

The perchlorate at 60° gave different degrees of brightness depending on the current density and pH. The plates became whiter as the pH was lowered and as the current was raised. Light gray deposits were obtained between pH 2 and 5 and 30 to 50 amp./sq. ft.; bright deposits were obtained at pH 2 and 3 between 77 and 144 amp./sq. ft. Plates between these ranges were semi-bright.

Plates obtained at 25° were, in all solutions, whiter in color than those at 60°; however, the range for satisfactory plates was not as great as at the higher temperatures. At the lower temperature some plates in all solutions cracked or peeled.

The chloride bath had the lowest voltage and the sulfate the highest.

The cathode efficiencies of the chloride bath were superior to those of the sulfate and perchlorate.

Anode corrosion rate was greatest in the chloride bath and lowest in the perchlorate.

Thick deposits made at a pH 4, 60° C., and a current density of 50 amp./sq. ft. showed the greatest treeing tendency of the sulfate bath. The chloride and perchlorate baths gave smooth plates free of nodules or trees. The chloride was dark, but the perchlorate had a whiter, brighter color.