

ELECTRODEPOSITION OF "BLACK NICKEL"

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In electrochemical practice coverings of "black nickel" have obtained rather wide use. Such coatings are used for decoration and for decreasing the coefficient of reflection. However, owing to certain difficulties in regulating the process, and to its small intensity, coatings of "black nickel" have, in a number of cases, been replaced by non-metallic coatings.

The literature information on the electrodeposition of "black nickel" [1,2,3] is fragmentary and incidental. Neither deposition of "black nickel" nor its composition have been studied sufficiently.

Extensive and rather complicated formulas for the electrolytes from which "black nickel" is deposited have been given, the use of which complicates the analytic and exact practical control of the process. In the present paper, the results of experiments to find a more simple electrolyte composition, which would permit the process to be intensified, and the best way of carrying out the electrodeposition of "black nickel", are reported.

For investigation of the conditions of deposition of "black nickel", the simplest electrolyte was chosen as a basis; this did not contain any substances which would complicate the study.

These substances include arsenic and cyanide compounds, which have been recommended in a number of cases.

The bath which had the simplest composition contained, in addition to nickel salts, sodium thiocyanate and zinc sulfate. The composition of such a bath, frequently recommended by many investigators, is (g/liter): $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ 60, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 7.5, NaCNS 15.

The electrolyte enabled operation only with small current densities (not higher than 0.15 A/dm^2). The deposits obtained from this bath were fragile and easily detached from the support.

To develop thick deposits of "black nickel" baths with a higher salt content of the following composition (g/liter) have been recommended: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 75, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ 45, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 38, NaCNS 15.

The work was carried out at $18-20^\circ$, a pH of 6.6-6.8, and a current density of 0.12 A/dm^2 .

In this electrolyte, as in the usual nickel baths, regulation of the acidity is very important if a high current efficiency is to be maintained.

For this purpose we buffered our solutions with H_3BO_3 . Sodium thiocyanate was replaced by the ammonium compound.

Thus the composition of the electrolyte was the following (g/liter): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 75, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ 45, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 40, NH_4CNS 15, H_3BO_3 25.

It is known that it is usual to heat the electrolyte in order to intensify the process.

Raising the temperature of the electrolyte from 44 to 55° enabled us to raise the current density to 1.3 A/dm², i.e., to accelerate the process by a factor of 8-9.

The effect of current density and temperature on the quality of the deposit was studied under these conditions.

Effect of current density and temperature on the quality of the deposit.

It was found that at 50° a deposit of gray nickel was obtained at small current densities of the order of 0.02-0.36 A/dm², which adhered very strongly to the support.

Increasing the current density changed the color of the deposit; it became darker and, within the limits of 0.38-1.30 A/dm², it was black. Simultaneously with the change in the color of the deposit, its quality changed as well. It became brittle. Increasing the current density above 1.30 A/dm² led to "scorching" of the deposit, i.e. metal was deposited as a powder.

When the temperature of the electrolyte was lowered from 50° to 20°, the limiting current densities at which "gray nickel" passed over into "black nickel" and the latter began to scorch, diminished; they gradually approached one another.

This dependence of the quality of the deposit on the temperature and current density is shown visually in Figure 1.

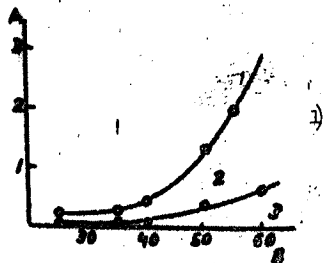


Fig. 1. Dependence of the quality of the deposit on the current density and temperature. A) Current density D_K (A/dm²). B) temperature (°C). 1) "scorched deposit"; 2) "black nickel"; 3) "gray nickel".

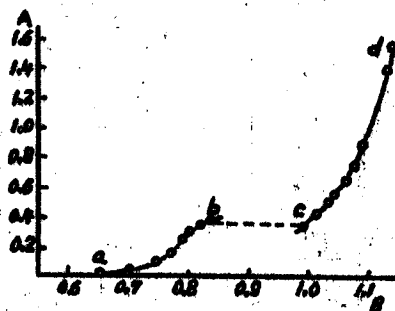


Fig. 2. Cathodic polarization curve. A) Current density D_K (A/dm²). B) Potential (V).

From Figure 1 it can be seen that raising the temperature considerably facilitates the deposition of "black nickel", by raising the range of current density in which the metal is deposited in this special form.

It is extremely interesting that the transition from "gray" to "black" nickel is not gradual, but discontinuous. This jump is clearly illustrated by the cathode polarization curve (Figure 2).

It can be seen from Figure 2 that the curve is typical of that obtained for the simultaneous electrodeposition of two metals, one of which has a potential considerably less negative than the other.

1) Figure 1. has been reproduced exactly as it appears in the original. Publisher.

It was supposed that curve ab on the graph should correspond to the separation of nickel, while curve cd corresponds to the preferential deposition of zinc. The horizontal portion bc should represent the transition from one process to the other. At 50° this inflection in the curve occurs at a c.d. of 0.36-0.38 A/dm².

Chemical analysis of "black" and "gray" nickel supports our conclusion (see Table).

D_k (A/dm ²)	Temperature (°C)	Composition of deposit	Current efficiency (%)	External appearance of deposit
		$\frac{Ni}{Ni + Zn}$ (%)		
0.05	50	86	5	Gray, adhering tightly to the support, tough
0.70	50	31	19	Black, adhering less tightly to the support, brittle

It is evident from the Table that there is a preferential deposition of nickel at a c.d. of 0.05 A/dm². The deposit, which was gray and which adhered strongly to the support (i.e. the electrode), contained 86% of nickel under these conditions, the remainder being zinc.

At a c.d. of 0.7 A/dm² predominantly zinc was deposited. In this case the nickel content fell to 31%. The amount of current which was wasted in liberating hydrogen increased considerably. The deposit was black and became more brittle.

In "black nickel" the sum total of zinc and nickel, in the weight of the deposit analyzed, was 57%. This forces us to the conclusion that it contains sulfur compounds. It is also possible that free sulfur and organic substances are present.

From the foregoing we came to the conclusion that the technical procedure for deposition of "black nickel" needs to be changed.

The process should start at a low c.d. of the order of 0.02-0.05 A/dm², permitting a dense adherent deposit of "gray nickel" to be laid as a foundation. The c.d. should be gradually raised and only toward the end of the process should it be brought up to the value necessary for the deposition of the "black" variety. This will ensure a better bonding of the deposit to the support.

A particularly strong bonding was obtained when the support had been previously nickel plated in the normal nickel plating bath. If the support is of steel, prior nickel plating appears to be a necessary condition for ensuring that the deposit adheres well and resists corrosion.

There is no exact information in the literature about the duration of the deposition of thin layers of "black nickel". Only in one case, for a bath with a low concentration of nickel, zinc, and thiocyanate, operating at a c.d. of 0.10-0.15 A/dm², is it recommended to carry on the operation for 25-30 minutes.

In cases where the nickel or zinc is used as a foundation deposit, this question is of no overriding importance, since the corrosion resistance is basically determined by the thickness of the foundation layer.

The time of electrolysis can be shortened to 15 minutes when the electrolyte proposed is used and the running conditions are those described earlier.

Experiments on the running of an industrial bath indicate that the deposition of the underlayer should be carried on for 10-12 minutes and only a further 3-5 minutes should be devoted to the deposition of "black nickel".

Prolonged deposition of "black nickel" increases the brittleness of the coating obtained.

No special experiments were made on the exhaustion of baths. An industrial bath, capacity 60 liters, operated without replenishment for 2 months, during which time about 2000 dm² were coated at an average c.d. of 0.5 A/dm², each coating taking 15-20 minutes.

The bath has a good throwing power, enabling complicated details to be covered.

The foundation must be polished in advance to get a lustrous black deposit.

SUMMARY

1. It is recommended that "black nickel" be deposited from a bath of the composition (g/liter): NiSO₄·7H₂O 75, NiSO₄·(NH₄)₂SO₄·6H₂O 45, ZnSO₄·7H₂O 40, NH₄CNS 15, H₃BO₃ 25.

The operating conditions should be: temperature 45-55°, c.d. 0.2-1.3 A/dm², pH of electrolyte 4.5-5.5; nickel anodes.

2. To ensure better adherence of the deposit to the support it is suggested that the deposition be made onto an underlayer of nickel plated out from the normal nickel plating bath, and to deposit "black nickel" at a gradually increasing c.d., starting at 0.2 and finishing at 1.3 A/dm².

3. The process may be controlled by varying the potential across the bath (from 0.8 to 2.0 V).

4. To get lustrous decorative coverings the parts concerned should be given a preliminary polish.

LITERATURE CITED

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