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ON THE QUESTION OF THE ELECTRODEPOSITION OF "BLACK NICKEL"

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In electroplating practice, the "black nickel" coating has come into quite wide use. It is employed both for decorative purposes and for reducing the coefficient of reflection. However, because of certain difficulties in controlling the process and because of the low rate at which it proceeds, "black nickel" plating has in many cases been replaced by non-metallic coatings.

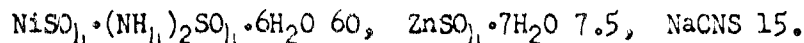
Information in the literature on the electrodeposition of "black nickel" [1,2,3] is of a fragmentary and casual nature. Neither the deposition process nor the constitution of "black nickel" has received adequate study.

As regards electrolytes for "black nickel" plating, there exists a large and quite complex array of formulae, the use of which makes it difficult to provide [a general procedure] for the analytic checking and precise regulation of the process. In the present paper we are giving the results of tests carried out for the purpose of determining the simplest electrolyte composition which would permit a speeding-up of the process; also some hints for improving the technology of "black nickel" electroplating.

Our procedure in investigating the conditions characterizing the deposition of "black nickel" was basically to select the simplest electrolytes, containing no substances which would complicate the study of the process.

Among such [complicating] substances are the arsenic and cyanide compounds, tartrate, licorice extract, etc., which are often recommended.

Simplest in composition is a bath containing (in addition to the nickel salts) sodium thiocyanate and zinc sulfate. A formula which has often been recommended for this bath, by many research workers, is as follows (g/l):



Here the electrolyte permits working only with small current-densities (not above 0.15 A/dm²). The deposit obtained with this bath is friable and comes away easily from the foundation-metal.

AD 682866

For building up thick deposits of "black nickel", a bath with a high content of the salts is recommended, having a composition as follows (g/l):

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 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 process is carried out at a temperature of 18-20°C, a pH varying from 6.6 to 6.8, and a current-density of 0.12 A/dm².

In this electrolyte, as in ordinary nickel baths, the regulation of the acidity is of great importance for maintaining a high current-efficiency.

To this end, we added a buffer of H_3BO_3 . Instead of sodium thiocyanate, we used ammonium thiocyanate in the bath.

Thus the composition of the electrolyte was as follows (g/l);

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 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 well known that heating of the electrolyte is often used as a means of forcing the process. Increasing the electrolyte temperature from 44 to 55°C enabled us to step up the current density to 1.3 A/dm², that is, to secure an 8-fold or 9-fold acceleration of the process.

In connection therewith, we made a study of the influence of current-density and temperature on the quality of the deposit.

Effect of Current Density and Temperature on the Quality of the Deposit.

An examination of the deposit quality, as related to the current density, at temperature 50°C, showed that at small cathode current densities, of the order of 0.02-0.36 A/cm², a coating of gray color was deposited, very strongly bonded to the foundation metal.

Increasing the current density causes a change in the color of the deposit: it becomes darker, and in the range of current-densities from 0.38 to 1.30 A/dm² the deposit is black. Simultaneously with the change in color there is also a change in its quality. The deposit begins to be friable. Increasing the current density above 1.30 A/dm² causes "scorching" of the coat, that is, the deposition of metals in a powdery form.

As the electrolyte temperature is lowered from 50° to 20°C, the two critical values of current-density, namely, that at which "gray nickel" goes over into "black nickel", and that at which the latter begins to "scorch", gradually approach each other.

This dependence of deposit quality on temperature and current-density is clearly illustrated in Fig.1.

From Fig.1 we see that the "black nickel" deposition process is easier to carry out at a higher temperature, since the range of current-densities in which "black nickel" is deposited increases with the temperature.

It is very interesting indeed that the transition from "gray nickel" to "black nickel" does not take place gradually, but discontinuously. This discontinuity is nicely shown by the curve of cathode polarization (Fig.2).

It is seen that Fig.2 is a typical curve of simultaneous deposition of two metals, one of which has a negative potential considerably less than the other.

We drew the conclusion that curve ab on the graph must represent a process of liberation of nickel, while curve cd represents a process mainly of zinc deposition. The flat step bc in the curve corresponds to the transition from one process to the other. At temperature 50°C this step is at current-density level 0.36 to 0.38 A/dm².

Chemical analysis of the "gray nickel" and the "black nickel" confirmed our conclusion (see table).

D _c (A/dm ²)	Temperature (in °C)	Composition of deposit	Current efficiency, hydrogen (in %)	Surface appearance of the deposit and its quality
		$\frac{\text{Ni}}{\text{Ni} + \text{Zn}}$ (in %)		
0.05	50	86	5	Deposit of gray color, solidly bonded to the foundation-metal, duc- tile.
0.70	50	31	19	Deposit of black color, less strongly bonded to the foundation-metal, friable.

From the table it is apparent that at a current density of 0.05 A/dm² there takes place predominantly a liberation of nickel. In the deposit, which is of gray color and strongly bonded to the foundation, the nickel content under these conditions is 86% of the total of nickel plus zinc.

When we work at a current density of 0.7 A/dm², it is mainly zinc that is liberated. The content of nickel drops to 31%. At the same time,

the current consumption and evolution of hydrogen markedly increase. The deposit has a black color and becomes more friable.

In the "black nickel", the total content of nickel plus zinc, relative to the weight of the deposit-sample analysed, amounts to 57%. This makes us think that the deposit consists of sulfide compounds. It is also possible that free sulfur and organic compounds are present.

From all this, we arrived at the conclusion that it would be a good idea to modify the technology of "black nickel" plating. The process should commence at a low current-density, of the order of 0.02 to 0.05 A/dm², which will permit the deposition of a solidly anchored coating of "gray nickel". Then the density is gradually increased, and only toward the end of the process should it be brought up to the levels necessary for deposition of "black nickel". In this way we insure a stronger anchoring of the coat to its foundation.

A particularly strong bonding is obtained if a preliminary nickel-plating is given, in the ordinary nickel bath. When plating on a steel foundation, the preliminary nickeling is a necessary condition to guarantee a solid anchoring of the coat and its resistance to corrosion.

In the literature, no precise indications are given re process times and coating thicknesses in "black nickel" plating. Only in one case, for a bath with a small content of nickel, zinc and thiocyanate, operated at a current density of 0.10 to 0.15 A/dm², is it specified that the process is to continue for 25 to 30 minutes.

This question is of no great importance when an undercoat of nickel or zinc is used, because the corrosion resistance will be chiefly determined by the thickness of the one or the other undercoating.

By using the suggested electrolyte and operating under the described conditions, it is possible to cut the electrolysis-time down to 15 minutes.

Experience with operating an industrial plating-bath suggests that the under-layer of "gray nickel" should be plated on for a period of 10-12 minutes, with only the last 3-5 minutes for the deposition of "black nickel".

A long period of "black nickel" deposition increases the friability of this layer.

We have not carried out any special performance tests. With an industrial bath of capacity 60 liters, which has now been worked for two months without any adjustments, about 2000 dm² of surface have been plated at a mean current density of 0.5 A/dm² and with a plating cycle of 15 to 20 minutes.

The bath has good dispersion properties, making it possible to plate objects of complicated shape.

To get a shiny black coating, a preliminary polishing of the foundation-metal is necessary.

CONCLUSIONS

1) It is recommended that "black nickel" plating be carried out with a bath of composition (g/l) as follows.

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 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.

Electrolytic operating conditions: temperature from 45 to 55°C, current density from 0.2 to 1.3 A/dm², pH from 4.5 to 5.5, nickel anodes.

2) To secure stronger bonding to the foundation-metal, it is suggested that an undercoat of nickel be laid down, from the ordinary nickel bath, and that the plating of the "black nickel" be carried out with a gradual increase of the current density from 0.2 to 1.30 A/dm².

Control (check) of the progress of the "black nickel" plating process may be maintained by supervision and adjustment of the voltage across the bath (from 0.8 to 2.0 V).

To get shiny decorative finishes, a preliminary polishing of the objects to be plated is required.

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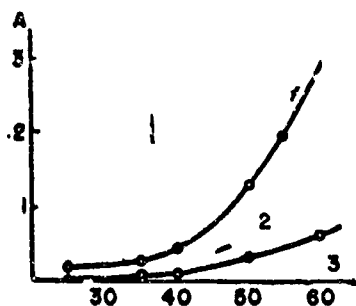


Fig.1. Dependence of deposit quality on current-density and temperature.

- A - current-density D_c (A/dm²)
 B - temperature (in °C)
 1. - "scorched" deposit
 2. - "black nickel"
 3. - "grey nickel"

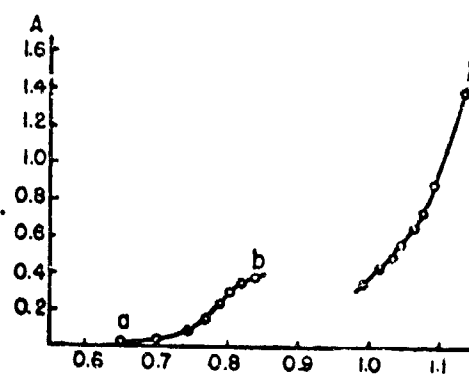


Fig.2. Curve of cathode polarization.

- A - current density D_c (A/dm²)
 B - potential (in volts)