

Electrodeposition of zinc-nickel alloy coatings: influence of a phenolic derivative

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The electroplating of Zn-Ni alloy films from a chloride bath has been studied under different plating conditions, both in the absence and presence of a phenolic derivative. Under the conditions examined, the electrodeposition of the alloys belonged to the anomalous type. The morphology and composition of the deposits varied with current density, temperature, bath composition and additive concentration. The results show that the additive modifies the structure and surface topography of the deposits to a large extent and produces smoother deposits. The corrosion resistance of the alloys has been analyzed by means of salt-spray tests.

1. Introduction

Electrodeposition of zinc-nickel alloys is of practical importance since they have a high degree of corrosion resistance and better mechanical properties than a pure zinc layer [1-3]. Comprehensive studies have been carried out on such electrodepositions from different baths, including sulphate [3-6], sulphate-sulphamate [7] and chloride baths [8]. Today there is a preference for chloride-based solutions although little reason for this can be found in the literature.

The purpose of the present investigation is to obtain smooth and bright zinc-nickel electroplates with good corrosion resistance from a chloride bath. Accordingly, we have made a systematic analysis of the different parameters influencing the deposition process: bath composition, current density and temperature. Initially we have investigated zinc-nickel alloys obtained from a pure electrolyte bath and also from one with an organic additive in the solution. Apart from judging the surface visually, the study also included an examination of its topography by scanning electron microscopy (SEM), a determination of deposit composition and testing of the corrosion resistance of the alloys, by the salt-spray technique.

2. Experimental details

Zinc-nickel alloy electrodeposits were usually obtained at 25°C. The electrolyte baths (of pH 4.8) were composed as follows: 135 g dm⁻³ zinc chloride; 30 g dm⁻³ boric acid; 155 g dm⁻³ sodium chloride; from 60.73 to 234.8 g dm⁻³ nickel chloride (NiCl₂ · 6H₂O); (from 15 to 58 g dm⁻³ of Ni²⁺).

In some experiments an organic additive (phenolic polyoxyethilenate derivative), developed by PREMA SA, was used in amounts between 0.5-7.0 g dm⁻³. The solutions were prepared using distilled water and reagent grade chemicals.

The experimental set-up for the electrodeposition process consisted of a rectangular methacrylate cell containing 250 cm³ of electrolyte solution. The cathode was a 4 × 4 cm² iron plate and the anodes of zinc had a total exposed area of 50 cm². The anodes were held in contact with the walls of the cell and the cathode was positioned midway between them. Electrodepositions were carried out under galvanostatic conditions to a constant thickness of 10 μm, under unstirred conditions. The cathodic potentials were measured relative to the saturated calomel electrode (SCE).

The cathode was mechanically polished with progressively finer grades of emery paper and, prior to deposition, was washed electrochemically in a strong basic solution. Before immersion the cathode was neutralized in a 10% HCl solution. After deposition, alloy films were washed with distilled water, dried with hot air and weighed.

The composition of each alloy was determined by means of a Unicam SP 1900 atomic absorption spectrophotometer. The morphology of the deposits formed was examined with a scanning electron microscope, JEOL/JSM 840.

For each electrodeposition condition at least three separate tests were carried out.

The percentage of nickel present in both baths and deposits, indicated by Ni_{sol} and Ni_{dep} respectively, was calculated as proposed by Brenner [9]. That is, accord-

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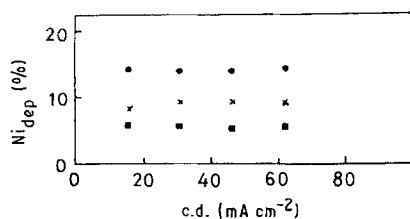


Fig. 1. Effect of current density (c.d.) on the percentage of nickel in zinc-nickel alloys electrodeposited from baths containing the following amounts of nickel: (■) 18.8, (×) 35.0 and (●) 47.2% of Ni^{2+} . For $t = 25^\circ\text{C}$.

ing to the relation

$$\% \text{Ni} = \frac{\text{mass Ni}}{\text{mass Ni} + \text{mass Zn}} \times 100$$

3. Results

The operating conditions used were chosen after working in different plating baths, in order to obtain reproducible zinc-nickel deposits.

The effect of cathodic current density on the deposits as studied by means of electroplating experiments at different current densities, between 15.6 and 62.5 mA cm^{-2} , keeping all other plating conditions constant. As seen in Fig. 1, alloy composition is not affected significantly by current density variations.

In order to ascertain the influence of deposit thickness on alloy composition, the deposits were electroplated to various thicknesses at 31.2 mA cm^{-2} . The composition of the alloy was almost constant throughout its thickness.

The influence of Ni^{2+} concentration on electroplate composition was also determined (see Fig. 2). The position of the curves in this figure show that, under the electrolysis conditions used, zinc is the most readily deposited metal and alloy deposition is of the anomalous type [9, 10], as the percentage of zinc, the less noble metal, in the deposit is always higher than its percentage in solution.

When the percentages of nickel in the deposits and

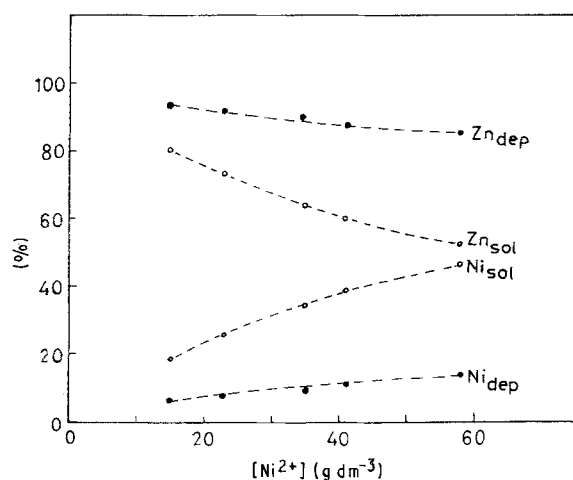


Fig. 2. The percentages of nickel and zinc in the alloys deposited from the baths: (●) metal percentage in the alloy; (○) metal percentage in the solution. At 25°C with c.d. = 31.2 mA cm^{-2} .

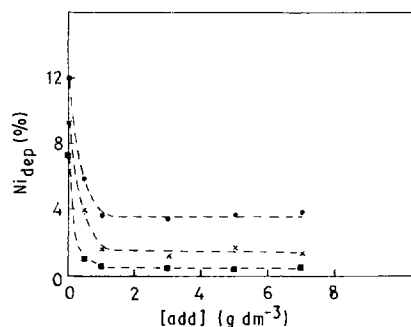


Fig. 3. Percentage of nickel in electrodeposited zinc-nickel alloys against the amount of phenolic derivative: (■) 24.2, (×) 35.0 and (●) 41.5% of Ni^{2+} . At 25°C with c.d. = 31.2 mA cm^{-2} .

in the solution are related, linear dependencies are obtained for all the deposition baths considered.

To study additive influence on the electrodeposition process, non-extreme experimental conditions have been selected: 31.2 mA cm^{-2} current density and nickel bath compositions of 23, 35 and 46 g dm^{-3} . Experiments were performed at different additive concentrations between 0.5 and 7.0 g dm^{-3} . Fig. 3 shows that small concentrations of addition agent produce significant changes in deposit composition: alloy composition changes rapidly with the initial additions of the agent and then tends toward a limiting value which was not appreciably affected by further increases in the concentration of the additive. The constant alloy composition observed from 1.0 g dm^{-3} of additive depends on the concentration of Ni^{2+} in the bath. The behaviour has been observed already in deposition of other alloys, as reported by Brenner [9].

Plating potentials were recorded at different time intervals during the electrodeposition process, both in the presence and absence of phenolic derivative. This potential shifted to more negative values when the organic derivative was added (see Table 1). This deposition potential also reaches a constant value for 1.0 g dm^{-3} of additive, as does deposit composition.

As is usual with this kind of additive, the phenolic derivative is adsorbed on the cathode surface in such a way that the deposition process is hindered, thus requiring a higher potential in order to reach a given rate of deposition. On the other hand, the presence of additive in the deposition bath modifies the electroplate composition, lowering the nickel content. This fact can be explained by the specific action of the additive on one of the metals, in the present case on

Table 1. Effect of the additive agent on the deposition potential for 35% of Ni^{2+} , $t = 25^\circ\text{C}$ and c.d. = 31.2 mA cm^{-2}

[Add]	E (mV against SCE)
0.0	-1095
0.5	-1120
1.0	-1141
3.0	-1145
5.0	-1145
7.0	-1145

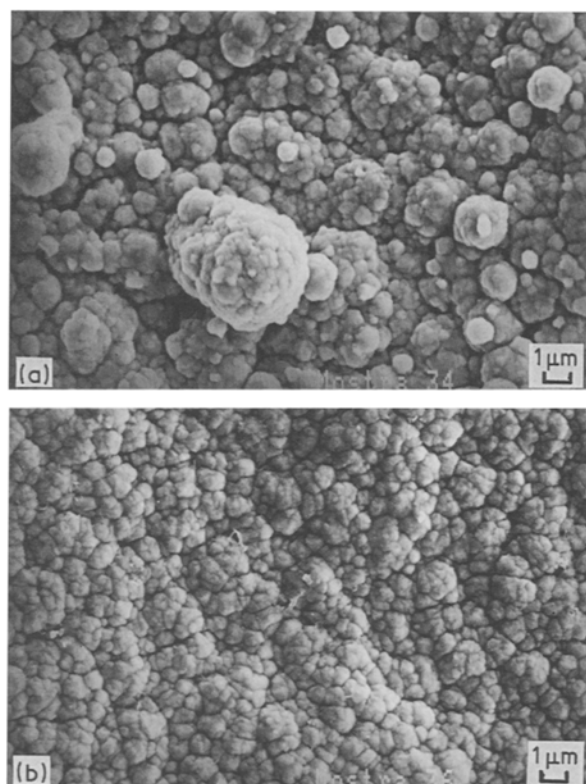


Fig. 4. Electrodeposited zinc-nickel alloy with: (a) $[\text{Ni}^{2+}] = 24.2\%$, $\text{Ni}_{\text{dep}} = 7.4\%$; (b) $[\text{Ni}^{2+}] = 35.0\%$, $\text{Ni}_{\text{dep}} = 9.2\%$, c.d. = 31.2 mA cm^{-2} at 25°C . Magnification: $3015\times$.

nickel, during codeposition. As can be seen in Fig. 3 and Table 1, both Ni percentage in the alloys and deposition potential level out when additive concentration reaches 1.0 g dm^{-3} . This behaviour suggests that, beginning at this concentration, the surface effect related to coverage of adsorbed additive on the cathode is always the same and the reduction process is unaffected by further additions of phenolic derivative.

The composition of the alloys has also been studied at different temperatures between 25° and 45°C . In this case the percentage of nickel in the deposits was found to increase significantly with rising temperature (Table 2).

3.1. Morphology of the deposits

The appearance of the zinc-nickel alloys depends on the nickel percentage in the bath and the presence or absence of additive. The deposits obtained without phenolic derivative were dark grey and dull, while those obtained with additive were more uniform, brighter and not so dark.

Table 2. Effect of temperature on Ni content (%) in the alloys for c.d. = 31.2 mA cm^{-2} , 35% of Ni^{2+} and 3.0 g dm^{-3} of phenolic derivative

Temperature ($^\circ \text{C}$)	% Ni_{dep}
25	1.2
30	3.5
35	6.6
40	10.3
45	15.3

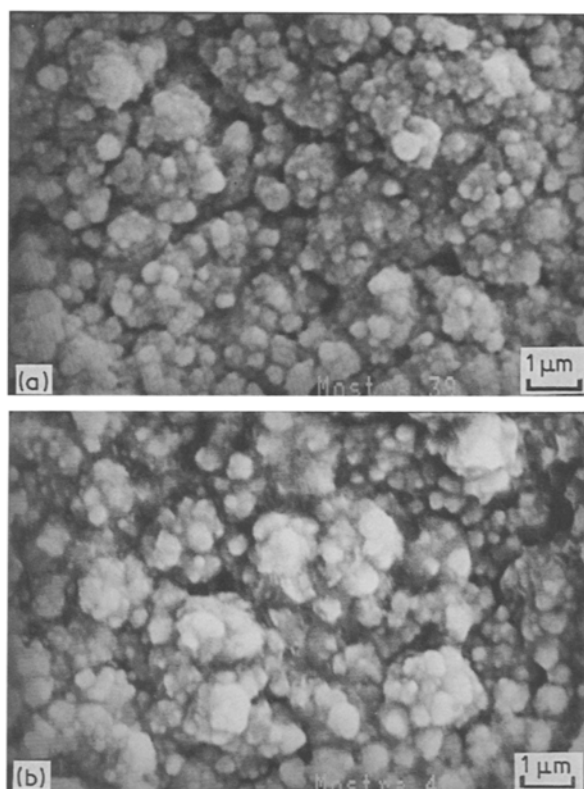


Fig. 5. Electrodeposited zinc-nickel alloy with $[\text{Ni}^{2+}] = 41.5\%$ and (a) $[\text{add}] = 1.0 \text{ g dm}^{-3}$, $\text{Ni}_{\text{dep}} = 2.7\%$; (b) $[\text{add}] = 7.0 \text{ g dm}^{-3}$, $\text{Ni}_{\text{dep}} = 3.2\%$. c.d. = 31.2 mA cm^{-2} at 25°C . Magnification: $5700\times$.

The surface SEM pictures of the electroplates obtained under different conditions resulting from the presence and absence of additive are quite revealing. Fig. 4 shows the structural details of some zinc-nickel deposits electroplated from the pure-electrolyte: (a) the deposits always had a nodular appearance, with grains of different size depending on the experimental conditions; (b) electroplates with a low percentage of nickel are irregular, with some pores and voids; when this percentage increases the deposit grain size is reduced; and (c) alloys obtained from the same solution, but with different current density, had the same medium grain size, but those obtained at low current densities were more uniform and compact.

In baths containing additive, the deposits showed a finer-grained texture and an increased nucleation density. Fig. 5 shows that the effect of the additive is to smooth the deposit and to refine the grain size. As has been observed with the % Ni_{dep} and the plating potential, alloys obtained with different additive amounts, from 1.0 g dm^{-3} , do not present significant differences, as can be seen in Fig. 5. The finer grain observed in this case can be related to the shift of cathodic potential; a decrease in the plating potential results in an increase of nucleation overgrowth and, hence, a more compact deposit with a finer grain size.

Moreover, when the photomicrographs of the cross-section of the zinc-nickel deposits obtained in the absence or presence of additive are compared (Fig. 6), smoother surfaces, without voids and prominences, are observed for additive-containing baths. In all cases, the effect of temperature is the same: the

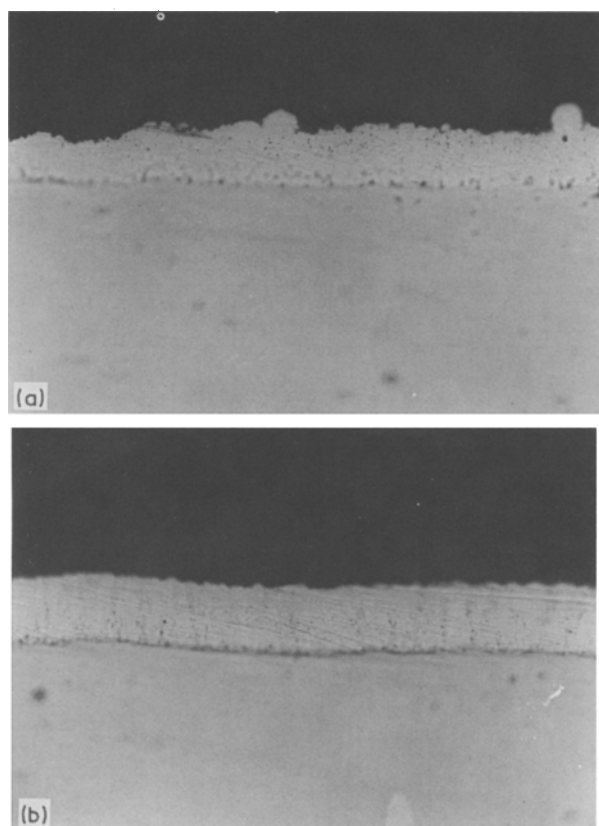


Fig. 6. Cross-section of zinc-nickel deposits. $[\text{Ni}^{2+}] = 35.0\%$, c.d. = 31.2 mA cm^{-2} at 25°C . (a) without additive, (b) with 5.0 g dm^{-3} of additive. Magnification: $250\times$.

grain size increases with increasing temperature, but electroplates obtained from additive-bearing baths are more compact (Fig. 7).

3.2. Corrosion resistance

The corrosion resistance of the electroplates obtained was evaluated by observing the propagation of both white and red rust formed on deposits $10 \mu\text{m}$ thick, which were tested in a 5% neutral salt-spray environment at 35°C . Results are expressed in percentage of the surface coated by rust as a function of exposure time.

White rust extension dependence on time is shown in Fig. 8. The appearance of this kind of corrosion does not depend significantly on electroplate composition and, in all cases, the percentage of surface coated by the rust reaches a constant value. This steady state is found to be dependent on alloy nickel content, as corroded surface percentage decreases with increasing amount of nickel in the deposit. This may be due to the formation of a more or less protective film that gradually reduces the corrosion rate.

Fig. 9 shows red rust evolution with time; in this case the curves have the characteristic form of a corrosion process which accelerates with time. In the absence of additive, corrosion resistance increases with the percentage of nickel in the deposit. While, as has been shown in Fig. 1, the nickel percentage in the alloys is independent of applied current density, the electroplates obtained at low current densities (up to 31.2 mA cm^{-2}) present a higher corrosion resistance.

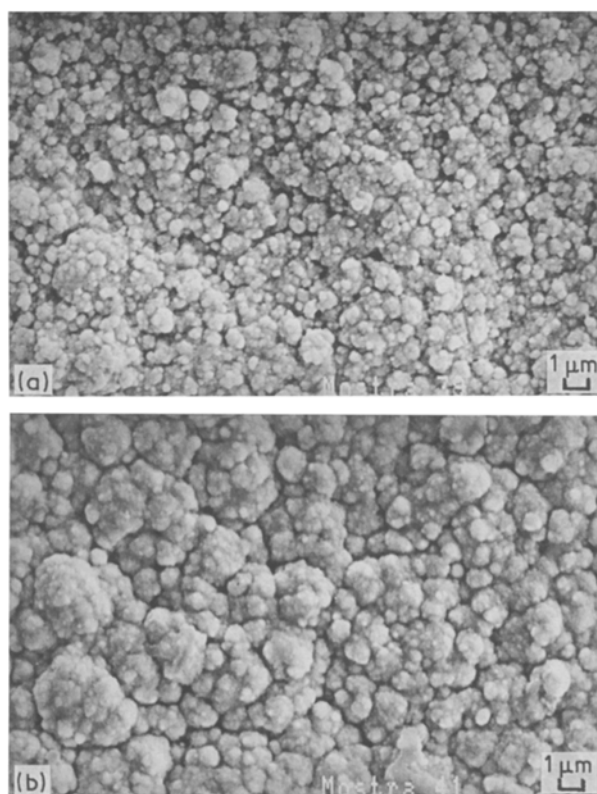


Fig. 7. Electrodeposited zinc-nickel alloys with $[\text{Ni}^{2+}] = 24.2\%$, $[\text{add}] = 3.0 \text{ g dm}^{-3}$, c.d. = 31.2 mA cm^{-2} . (a) $\text{Ni}_{\text{dep}} = 0.50\%$ at 25°C ; (b) $\text{Ni}_{\text{dep}} = 7.15\%$ at 40°C . Magnification: $3105\times$.

This fact can be related to a higher degree of uniformity and compactness observed in these electroplates.

When the phenolic derivative is added, alloy nickel content decreases, as has been mentioned above, but corrosion resistance is improved (curve 3 in Fig. 9 corresponds to an alloy obtained without additive and having a high nickel content, but its deposit does not have the best corrosion resistance). For each of the deposition baths studied, the nickel percentage of the deposits attains a constant value from concentrations of additive higher than 1.0 g dm^{-3} (Fig. 3) and it has been observed that the corrosion resistance of these deposits is also similar. The alloys obtained from additive concentrations lower than 1.0 g dm^{-3} have a lower corrosion resistance although they have a higher Ni percentage (curves 4 and 5, Fig. 9). When the different deposition baths are compared, the corrosion

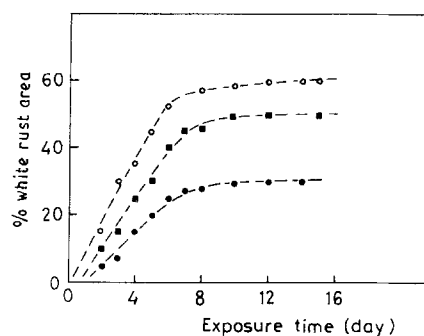


Fig. 8. Propagation rate of white rust on the Zn-Ni alloys electroplated on iron during the salt-spray test. c.d. = 31.2 mA cm^{-2} : (O) $[\text{Ni}^{2+}] = 24.2\%$, $[\text{add}] = 1.0 \text{ g dm}^{-3}$ at 25°C , $\text{Ni}_{\text{dep}} = 0.6\%$; (■) $[\text{Ni}^{2+}] = 35.0\%$, $[\text{add}] = 1.0 \text{ g dm}^{-3}$ at 25°C , $\text{Ni}_{\text{dep}} = 1.6\%$; (●) $[\text{Ni}^{2+}] = 35.0\%$, $[\text{add}] = 3.0 \text{ g dm}^{-3}$ at 35°C , $\text{Ni}_{\text{dep}} = 6.6\%$.

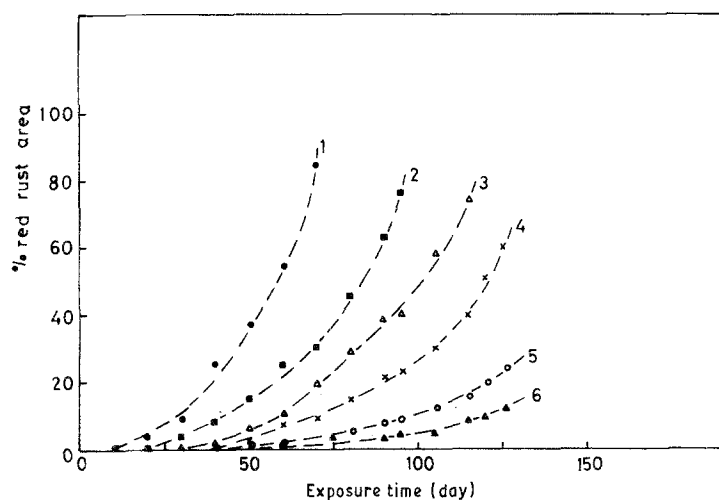


Fig. 9. Propagation rate of red rust on the zinc-nickel alloys electroplated on iron during the salt-spray test. c.d. = 31.2 mA cm^{-2} . Curve 1: $[\text{Ni}^{2+}] = 18.8\%$, $[\text{add}] = 0.0 \text{ g dm}^{-3}$ at 25°C , $\text{Ni}_{\text{dep}} = 6.0\%$; curve 2: $[\text{Ni}^{2+}] = 24.2\%$, $[\text{add}] = 3.0 \text{ g dm}^{-3}$ at 25°C , $\text{Ni}_{\text{dep}} = 0.5\%$; curve 3: $[\text{Ni}^{2+}] = 47.2\%$, $[\text{add}] = 0.0 \text{ g dm}^{-3}$ at 25°C , $\text{Ni}_{\text{dep}} = 14.0\%$; curve 4: $[\text{Ni}^{2+}] = 38.7\%$, $[\text{add}] = 0.5 \text{ g dm}^{-3}$ at 25°C , $\text{Ni}_{\text{dep}} = 5.0\%$; curve 5: $[\text{Ni}^{2+}] = 41.5\%$, $[\text{add}] = 3.0 \text{ g dm}^{-3}$ at 25°C , $\text{Ni}_{\text{dep}} = 3.8\%$; curve 6: $[\text{Ni}^{2+}] = 35.0\%$, $[\text{add}] = 3.0 \text{ g dm}^{-3}$ at 45°C , $\text{Ni}_{\text{dep}} = 10.3\%$.

resistance increases with the Ni content of the alloys. An increase in the deposition temperature increases the nickel percentage in the deposits and, thus, favours their corrosion resistance (curve 6, Fig. 9).

4. Conclusions

The electroplating of zinc-nickel alloys from the bath solutions under investigation, in the absence and presence of phenolic derivative, exhibits the phenomenon of anomalous codeposition. The electroplates obtained without the addition of agent have good corrosion resistance, particularly those with higher nickel content, but they are dull and irregular. When the phenolic derivative is added to the deposition bath, the general aspect of the electroplates is improved and their corrosion resistance is also good, in spite of the lower nickel percentage yield. The additive causes a significant change in deposit surface topography, as well as in grain size.

From the corrosion tests with the salt spray, it may be concluded that not only does corrosion resistance depend on the percentage of nickel in the deposits, but also it depends on their morphology, in such a way that the electroplates which exhibit a uniform distribution of grains of the same size are those with better corrosion resistance, even with a lower nickel content.

The use of an organic additive in the electrolyte is essential when electroplating Zn-Ni alloys but, as expected, experimental conditions must be optimized

by adding some other organic additive in order to improve the smoothness and brightness of the deposits.

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