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Zinc–nickel coatings: relationship between additives and deposit properties

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The electroplating of zinc–nickel alloys from a chloride bath containing two brighteners (a phenolic derivative and an unsaturated aromatic compound) and a levelling agent (an aromatic carboxylate) has been studied under different plating conditions. The composition and morphology of the alloys depended on the concentration of all the additives and also on the temperature. As a general effect, these additives smooth the deposit and refine the grain size. By means of scanning electron microscopy, it was possible to classify the deposit morphologies according to the type and concentration of the additives. The resistance of the alloys to corrosion was studied by means of a neutral salt-spray test.

1. Introduction

It is well recognized that alloy coatings on base metal substrates can provide desirable surface properties with respect to corrosion protection and mechanical properties. It is also known that in the electrodeposition of these metalic coatings the use of one additive or a combination of them allows deposits with more corrosion resistance and better aspect to be obtained [1–7].

At present, electrodeposited Zn–Ni alloy coatings are of high technological interest [8–20]. The influence of a phenolic derivative as a brightener on the electrodeposition of zinc–nickel alloys was the subject of a previous study by our group [21]. It was observed that this additive improved the appearance of the deposits and also their corrosion resistance. In order to obtain smooth and bright deposits with satisfactory corrosion resistance we have analysed, in the present study, the influence of three additives on Zn–Ni alloys: the phenolic derivative used previously, a new brightener (B2, an unsaturated aromatic compound) and a levelling agent (LA, an aromatic carboxylate), the additive system designed by Prema S.A.

Moreover, the zinc–nickel coatings obtained under different plating conditions have been chromated in acid solutions to optimize the quality of the deposits and to compare the corrosion resistance of the electroplates with and without the passivating film.

2. Experimental details

The zinc–nickel electroplates were obtained at a constant current density of 31.2 mA cm^{-2} and from a bath of the following composition. Zinc chloride: 135 g dm^{-3} (65 g Zn^{2+} dm^{-3}), nickel chloride: 142 g dm^{-3} (35 g Ni^{2+} dm^{-3}), boric acid: 30 g dm^{-3}, sodium chloride: 156 g dm^{-3}, pH: 4.8.

In this study, the bath contained different concentrations of the phenolic derivative used previously [21], the B2 unsaturated aromatic compound and the LA aromatic carboxylate. Table 1 summarizes the compositions of the deposition baths.

Except for the case where the effect of temperature was studied, all experiments were carried out at 25° C. The other experimental details were the same as described previously [21], but in the present case one electroplate obtained for each plating condition was

Table 1. Concentrations of additives (g dm^{-3}) used in the electrodeposition baths.

Phenolic derivative	*Second brightener (B2)*	*Levelling agent (LA)*
1.0	0.05	
	0.10 (A)	0.0–0.25
	0.15	
	0.25	
3.0	0.10	0.0 and 0.01
	0.30	0.0 and 1.0
	0.50	0.0 and 1.0
5.0	0.05	
	0.10	
	0.15	
	0.25 (B)	0.0–1.5
	0.40	
	0.50 (D)	0.0–1.5 (C)
	0.75	
7.0	0.50	0.0–2.0
	0.75	0.0 and 2.0 (E)
	1.00	0.0 and 2.0

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chromated by immersion for 30 s in a chromating solution of the following composition. Potasium dichromate: 10 g dm^{-3}, sulphuric acid: 2 g dm-3, pH: 1.7.

After chromating, the deposits were rinsed in distilled water, dried with warm air and subjected to the salt-spray test, after ageing at room temperature for 24 h.

3. Results

In the previous work [21] it was shown that deposit characteristics such as composition, morphology or corrosion resistance were similar for all the alloys obtained from a bath with a phenolic derivative concentration higher than 0.5 g dm^{-3}. In view of these results, two concentrations of this additive (1.0 and 5.0 g dm^{-3}) were selected in the present case to study the influence of the second brightener (B2) and that of the levelling agent (LA).

3.1. *Effect of the second brightener*

The concentration of B2 was varied between 0.05 and 0.25 g dm^{-3} when considering a bath containing 1.0 g dm^{-3} of the phenolic derivative. Without this second additive and with a Ni^{2+} concentration in the bath of 35 g dm^{-3}, the percentage of nickel in the deposits was about 1.6% [21]. By adding the second brightener and independently of its concentration, this percentage was in all cases about 1.5%. The zinc-nickel electroplates obtained under these conditions were rather dull or slightly bright and after chromating most of them were dark blue-green.

The influence of the second additive was studied from 0.05 to 0.75 g dm^{-3} while keeping the phenolic derivative concentration at 5.0 g dm^{-3}. In this case a dependence between the percentage of nickel in the deposits and the additive concentration was observed (Fig. 1), in such a way that the $\%Ni_{dep}$ decreased with the increase of the B2 concentration up to 0.25 g dm^{-3}, attaining a constant value of about 0.75%.

The deposits obtained under these conditions were generally better than those obtained from 1.0 g dm^{-3} of phenolic derivative, and their appearance was improved if the concentration of the second brightener was increased. After the chromating process, the electroplates were dark yellow-green and the most uniform were those obtained with the highest B2 concentrations.

3.2. *Effect of the levelling agent*

With 1.0 g dm^{-3} of phenolic derivative, the deposit with the best appearance was obtained by using 0.1 g dm^{-3} of the second additive (Solution A in Table 1). As a consequence, this bath composition was selected to analyse the influence of the levelling agent on the deposits.

Solution A was modified by varying the LA concentration between 0.05 and 0.25 g dm^{-3}. The nickel percentage in all the alloys fell to 0.8%, independently of the LA concentration in the deposition bath. The electroplates obtained under these conditions were dull and rough and their appearance was worsened as the LA concentration increased. After the chromating process, the films obtained were always dark and not uniformly coloured.

When the plating bath contained 5.0 g dm^{-3} of the phenolic derivative the electroplates, obtained using B2 concentrations higher than 0.15 g dm^{-3}, were all bright and uniform. Thus, the solution with 0.25 g dm^{-3} of the second brightener (Solution B in Table 1) was selected to study the effect of the levelling agent.

Solution B was modified by varying the LA concentration between 0.02 and 1.5 g dm^{-3}. This analysis demonstrates that the nickel content of the deposits also decreased with the LA concentration (Fig. 2), reaching a constant value of 0.25% at high levelling agent concentrations. All the alloys obtained with these bath compositions were very bright and uniform and their brightness increased with the LA bath concentration. The passivating chromate films observed for these electroplates were always uniformly coloured, being dark when obtained from low LA concentrations and very light for those corresponding to higher amounts of levelling agent.

After this study, it was concluded that, for a bath containing 35 g dm^{-3} of Ni^{2+}, a concentration of phenolic derivative of 1.0 g dm^{-3} is not enough to obtain good zinc-nickel electroplates. By adding the second brightener the appearance of the deposits is slightly improved, but this improvement can not be enhanced with the addition of the levelling agent.

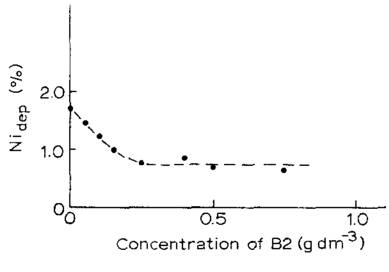

Fig. 1. Percentage of nickel in electrodeposited zinc-nickel alloys versus the concentration of the second brightener, for a concentration of phenolic derivative of 5.0 g dm^{-3}.

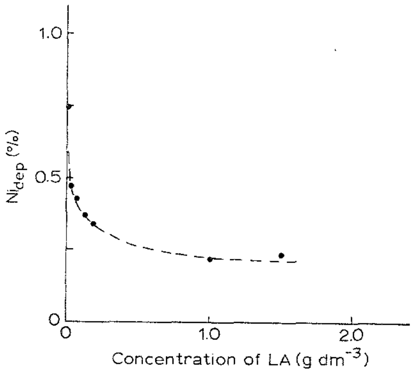

Fig. 2. Percentage of nickel in electrodeposited zinc-nickel alloys against the concentration of the levelling agent for a concentration of phenolic derivative of 5.0 g dm^{-3} and 0.25 g dm^{-3} of B2.

On the other hand, it is possible to obtain very uniform and bright zinc–nickel alloys with 5.0 g dm^{-3} of phenolic derivative by adding only the second brightener or also very small concentrations of the levelling agent. Under these conditions of 5.0 g dm^{-3} of phenolic derivative, if the bath only contained this additive and the B2 in a proportion lower than 30/1 or also with very small amounts of LA, it was observed that the electroplates presented some similarities: they had a nickel content of about 0.75% and the passivating films had a dark yellow-green hue. When the levelling agent concentration was higher, some regularities were also observed on the deposits: if the relationship phenolic derivative/B2/LA lay between the intervals 3.0–5.0/0.2–0.5/1, all the electroplates were mirror bright, had a %$\mathrm{Ni_{dep}}$ of about 0.25% and the chromating films were light in colour.

3.3. *Additional experiments*

To confirm that the deposits had the same properties over certain ranges of additive concentrations, different baths were prepared with 3.0 and 7.0 g dm^{-3} of phenolic derivative and the second brightener, in such a way that the relation between their concentrations was always lower than 30/1. The results obtained with these experiments were in agreement with those mentioned above. The alloys presented the same appearance and had the same nickel content.

The other interval of additive concentrations was also studied with 3.0, 5.0 and 7.0 g dm^{-3} of phenolic derivative and different amounts of B2 and LA, always in the relation 3.0–5.0/0.2–0.5/1 and also in this case the appearance and composition of the alloys corresponded to what was expected.

Moreover, with solutions C and D of Table 1, experiments were performed with a Hull cell to verify whether the appearance of the deposits was maintained over a wide range of current densities. With an applied current intensity of 1.0 A and after the chromating process, the deposit obtained from solution B (phenolic derivative and B2 in a relation 20/1) presented the same characteristics from 10 to 70 mA cm^{-2}. At lower current densities the nickel contents of the deposits was so high that it was completely inert to the passivating solution. On the other hand, the deposit obtained from solution C (relation phenolic derivative, B2 and LA of 3.3/0, 33/1) was very uniform over the range of current densities, 0.5 to 70 mA cm^{-2}.

3.4. *Effect of temperature*

The effect of the deposition temperature on the zinc–nickel alloys was studied for two particular bath compositions, the first only containing both brighteners (Solution D in Table 1) and the second with all the additives (Solution E in Table 1). The effect of increasing the bath temperature was the same as that observed in other cases of anomalous codeposition (Table 2), that is an increase of the nickel percentage on the deposit [21, 8].

Table 2. Effect of the temperature on the percentage of nickel of the deposits obtained from solutions C and D of Table 1

Solution	*Temperature (° C)*	*$\mathrm{Ni_{dep}}$ (%)*
D	25	0.7
	35	2.7
	45	8.9
	50	15.2
E	25	0.2
	30	0.2
	35	0.3
	40	0.6
	55	1.1
	60	1.5

The effect of the temperature on the composition of an alloy deposited in anomalous codeposition is determined by two opposing influences: polarization and diffusion [11, 22]. By increasing the temperature, the first effect tends to increase the content of the more noble metal in the deposit, while the second tends to favour the deposition of the less noble. With the plating conditions used in this work, it seems that the influence of polarization predominates over that of diffusion and the nickel content of the deposits always increases by raising the temperature of the plating bath.

Although both solutions D and E presented the same general behaviour, the increase of the %$\mathrm{Ni_{dep}}$ was much greater for solution D, which had no levelling agent. In this case at 35° C the nickel content of the deposits was about 3%, while at 50° C the alloys had a 15.2% of nickel and they were completely inert to the chromating solution.

The increase of the nickel content was much more gradual if solution E was used and at 60° C the electroplates only had 1.5% of nickel. The passivating films were very uniform and light yellow-green in all cases.

3.5. *Morphology of the deposits*

The structures of the alloys were examined by scanning electron microscopy (SEM). It was observed that the morphology of the deposits depended on the amount of additives and also on the relationship between their concentrations.

For low concentrations of the second additive, when the bath contained 1.0 or 3.0 g dm^{-3} of phenolic derivative the deposit consisted of elongated dihedral grains oriented at random (Fig. 3a). For 5.0 g dm^{-3} of phenolic derivative the grains were not elongated, but still presented sharp edges (Fig. 3b), while for 7.0 g dm^{-3} of this additive the grains always had a nodular appearance. The effect of increasing the second additive concentration was the same for all the amounts of phenolic derivative: the grains became nodular and their size was gradually reduced.

When the third agent was added to a bath containing 1.0 g dm^{-3} of phenolic derivative and the second brightener, the deposits became very rough, as mentioned above. When the concentration of phenolic

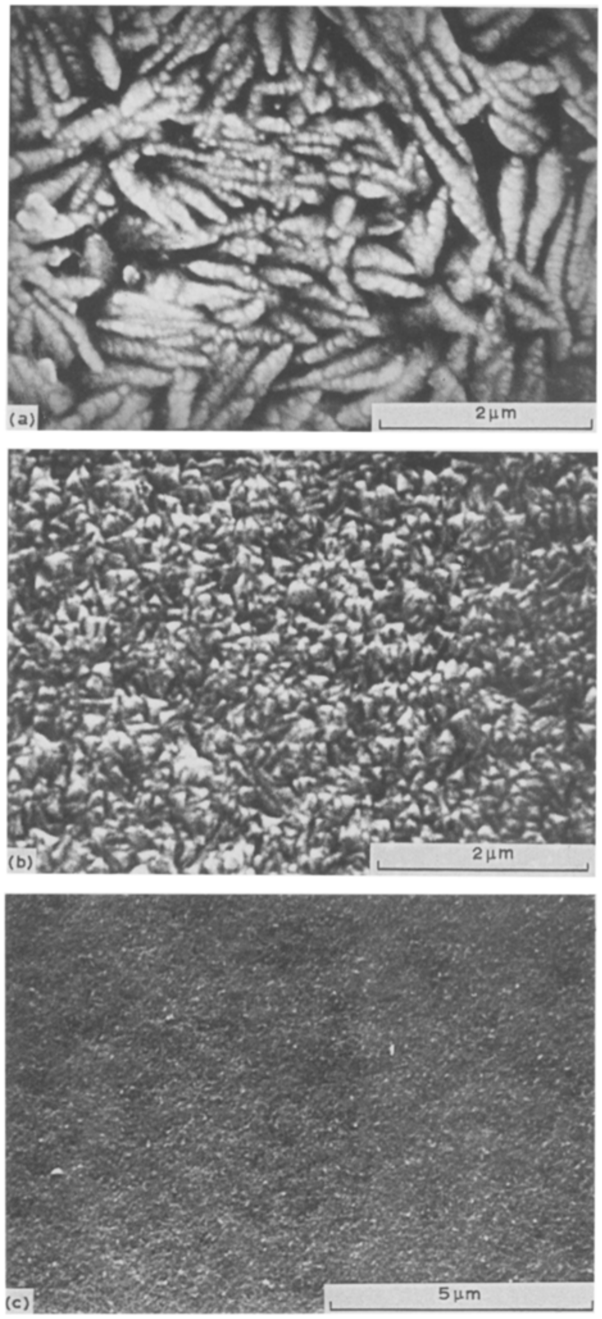

Fig. 3. Electrodeposited zinc-nickel alloys. (a) [phenol. der.] = 3.0, [B2] = 0.1 g dm^{-3}. Magnification 13400 ×; (b) [phenol. der.] = 5.0, [B2] = 0.05 g dm^{-3}. Magnification 13400 ×; (c) [phenol. der.] = 5.0, [B2] = 0.25, [LA] = 1.5 g dm^{-3}. Magnification 6700 ×.

derivative was increased the influence of the third additive on the deposit structure was always the same: it reduced the grain size, in such a way that at high LA concentrations the grain sizes were not measurable (Fig. 3c).

It has been proposed [23] that brighteners are adsorbed at points of low overpotential, and inhibit lateral growth and, as a result, influence the grain structure. In the previous work [21] it was observed that the phenolic derivative increased the uniformity and compactness of the deposits, but the grain always had a nodular appearance. In the present case, at low concentrations of both the first and the second additives the deposit grains were elongated and this could be explained by a partially inhibited lateral growth of crystallites. Thus, it seems that these additives both act as brighteners because both level up grain sizes, but it is the second which has the highest influence on the deposit structure.

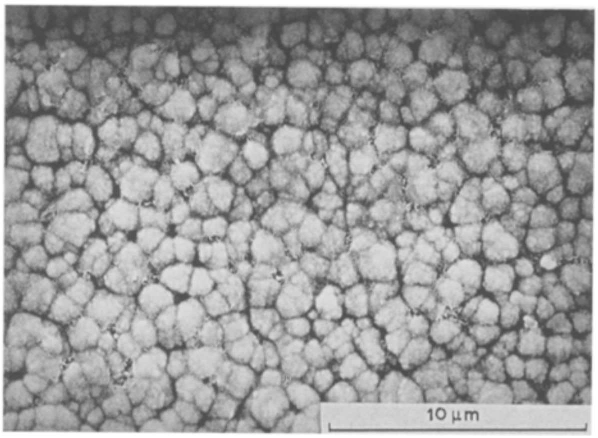

Fig. 4. Effect of temperature on the morphology of zinc-nickel deposits obtained from solution D of Table 1. Temperature 50° C. Magnification 3350 ×.

On the other hand, the roughness observed in some deposits has been attributed to hydrogen codeposition. The phenolic derivative used in these baths acts as a brightener and, moreover, as a wetting agent, reducing the surface tension at hydrogen bubbles. When the bath contains low concentrations of this additive (1.0 g dm^{-3}) it seems that the levelling agent cancels out this wetting effect and the occluded hydrogen bubbles cause pitting during the alloy deposition. When the concentration of phenolic derivative was increased it was large enough to prevent hydrogen codeposition, even at high LA concentrations and, in these cases, the effect of this levelling agent was only to reduce the grain sizes.

The effect of increasing the temperature in solution D promoted an increase in the grain size and in the compactness of the alloys (Fig. 4), while for solution E, which contained a high LA concentration, the grain size was always non measurable, even at 60° C.

The SEM pictures of the chromating films showed differences between those which are light coloured (Fig. 5a, the Zn-Ni alloys had non measurable grain sizes) and those which had a dark hue (Fig. 5b). The passivating films were always cracked, but the film was more uniform and the cracks were more regular in the first case.

3.6. *The deposition potential*

When the phenolic derivative was added to the bath a shift of the deposition potential to more negative values was observed [21]. The same behaviour was also observed with the second and third additives, the shift caused by the addition of the levelling agent being greater. This fact can be observed in Table 3, which shows the plating potentials obtained for baths with different amounts of additives.

The dependence of the deposition potential on the concentration of the second and third additives was also similar to that observed with the phenolic deriva-

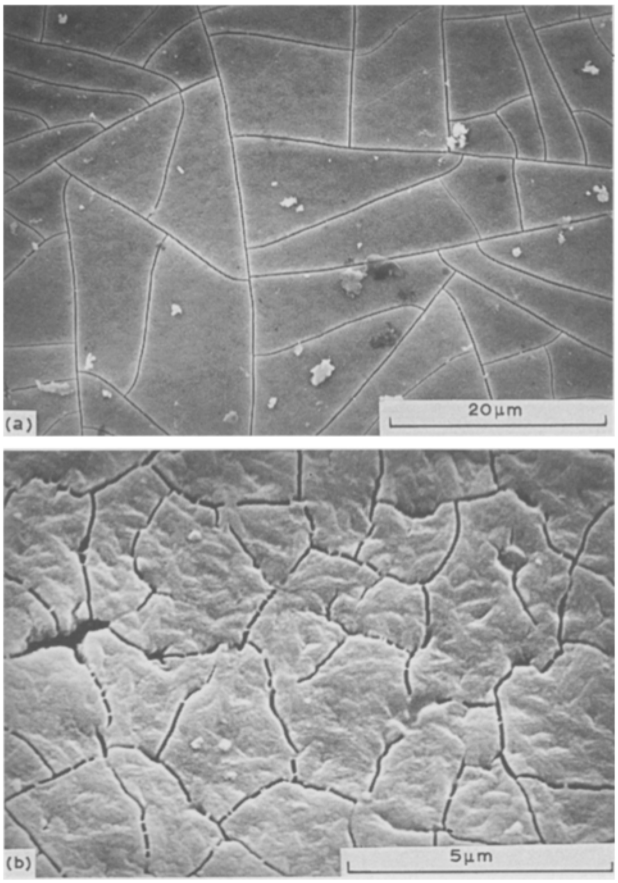

Fig. 5. Microstructure of chromate films. (a) [phenol. der.] = 3.0, [B2] = 0.3, [LA] = 1.0 g dm^{-3}. Magnification 1340 ×; (b) [phenol. der.] = 5.0, [B2] = 0.25, [LA] = 0.05 g dm^{-3}. Magnification 6700 ×.

tive [21], reaching a constant value as does the nickel percentage of the alloys (Fig. 1, 2). This fact suggested that the influence of the second brightener and that of the levelling agent on the deposition process could also be a consequence of their possible adsorption on the cathode surface. These hypotheses could be confirmed with further studies (cyclic voltammetry, capacitance measurements, . . .) relative to the role of these additives in the deposition mechanism.

The variation of the plating potential was in agreement with the morphology of the alloys, since a decrease in the deposition potential results in an increase of nucleation over growth and, hence, the deposits were more compact with a finer grain size. The most negative plating potentials always corresponded to the electroplates with non measurable grain sizes.

Table 3. Effect of the additive concentrations on the deposition potential.

Phenolic derivative (*g dm*$^{-3}$)	*Second brightener* (*B2*) (*g dm*$^{-3}$)	*Levelling agent* (*LA*) (*g dm*$^{-3}$)	(*E*) (*mV*)
0.0	0.00	0.00	−1095
5.0	0.00	0.00	−1145
5.0	0.10	0.00	−1150
5.0	0.25	0.00	−1160
5.0	0.25	0.05	−1175
5.0	0.25	1.50	−1220

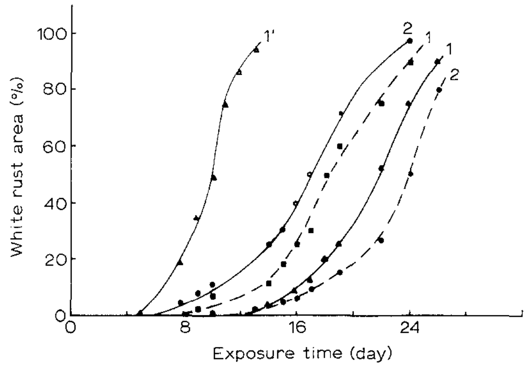

Fig. 6. Propagation rate of white rust on the chromated and nonchromated (1′) Zn–Ni alloys during the salt-spray test for a [phenol. der.] = 5.0 g dm^{-3}. Broken lines: (1) [B2] = 0.25; (2) [B2] = 0.75 g dm^{-3}. Solid lines [B2] = 0.25 g dm^{-3}. (1) [LA] = 0.02; (2) [LA] = 1.5 g dm^{-3}; 1′) same conditions than solid line 1.

3.7. *Corrosion resistance*

The corrosion resistance of the alloys, passivated and not passivated with the chromating film, was evaluated by observing the propagation of both white and red rust formed on the deposits, tested in a 5% neutral salt-spray environment at 35° C. Results are expressed in percentage of surface coated by the rust as a function of the exposure time.

In the previous work [21], it was observed that the corrosion resistance of the alloys improved with the addition of the phenolic derivative, and this resistance was very similar for all the electroplates obtained from concentrations of this additive higher than 0.5 g dm^{-3}. In the present case, the addition of a new brightener and a levelling agent also generally improved the corrosion resistance of the alloys.

All the electroplates obtained from a bath with 1.0 g dm^{-3} of phenolic derivative gave poor corrosion resistance, while it was observed for other conditions that both white and red rust followed the same general behaviour.

– At a given concentration of phenolic derivative, the corrosion resistance increased with increasing concentration of the B2 additive (broken lines 1, 2 of Fig. 6 and 1–3 of Fig. 7).

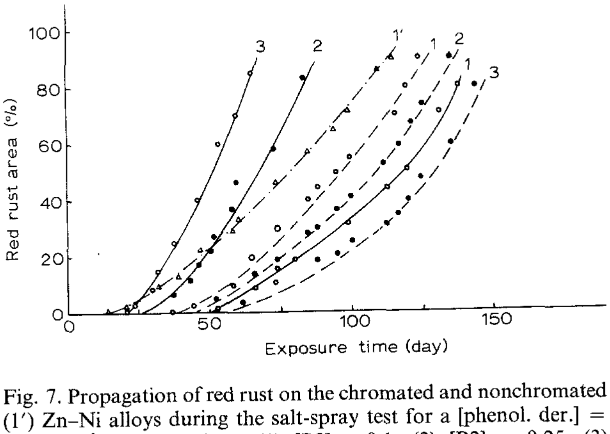

Fig. 7. Propagation of red rust on the chromated and nonchromated (1′) Zn–Ni alloys during the salt-spray test for a [phenol. der.] = 5.0 g dm^{-3}. Broken lines: (1) [B2] = 0.1; (2) [B2] = 0.25; (3) [B2] = 0.75 g dm^{-3}. Solid lines [B2] = 0.25 g dm^{-3}: (1) [LA] = 0.05; (2) [LA] = 0.1; (3) [LA] = 1.0 g dm^{-3}; 1′) same conditions than solid line 1.

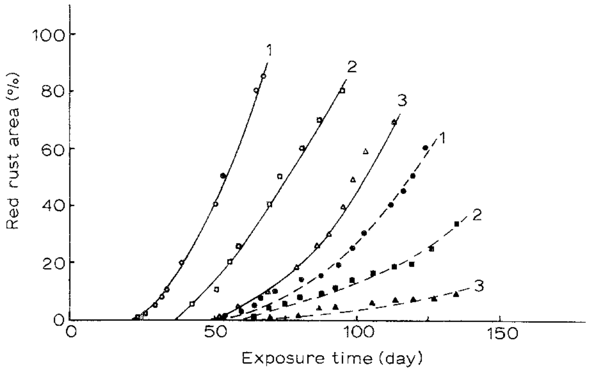

Fig. 8. Effect of the temperature on the propagation of red rust for chromated Zn–Ni alloys during the salt-spray test. Broken lines, solution D of Table 1: (1) 25; (2) 45; (3) 50° C. Solid lines, solution E of Table 1: (1) 25; (2) 40; (3) 55° C.

– Small amounts of LA also favoured the corrosion resistance of the alloys, but the resistance worsened with successive additions of this levelling agent (solid lines 1, 2 of Fig. 6 and 1–3 of Fig. 7).

Thus, the corrosion resistance of these electroplates was more related to their morphology than to their composition. The best behaviour was obtained with the alloys which had nodular grains of measurable size, while those which had elongated or non measurable grains always gave worse corrosion resistance.

The influence of chromate films on white rust was found to be the same for all electroplates, independently of the colour of the film. The passivating film delayed the appearance of white rust between 7 and 9 days and the corrosion rate was the half that observed without the chromate film (solid lines 1 and 1′ of Fig. 6).

The chromate film also caused a delay in the appearance of the red rust, but the rate of corrosion was similar to that observed without the passivating film (solid line 1 and curve 1′ of Fig. 7). It was found in this case that the delay was more significant for the electroplates with a dark chromating film (nodular and measurable grains), meaning that the passivating film improved the corrosion resistance of all the electroplates, but particularly that of the alloys which presented the best corrosion resistance without the chromate film.

Finally, an increase of the deposition temperature always improved the corrosion resistance of the alloys (Fig. 8), but this effect was greater when it was accompanied by a significant increase of the percentage of nickel in the alloys.

4. Conclusions

Zinc–nickel electroplates have been obtained from a chloride bath by adding a new brightener and a levelling agent, which improved the apearance and the corrosion resistance of the alloys.

Varying the relationship between the additive concentrations, two intervals have been established that lead to two kinds of electroplates.

– High concentrations of all additives gave alloys with mirror bright deposits but poor corrosion resistance.

– When the concentration of phenolic derivative in solution was between 3.0–7.0 g dm^{-3}, with a relation phenolic derivative/B2 lower than 30 : 1, or also with very small amounts of LA, it was possible to obtain bright electroplates which gave very good corrosion resistance. These electroplates present a good corrosion resistance in spite of the low nickel percentage in the alloy. This behaviour was also observed for Zn–Ni coating obtained with other organic additives [19].

As the deposit characteristics mainly depended on the concentration of additives, further study is required to determine the role of these compounds in the deposition of zinc–nickel alloys.

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