Influence of organic additives on the behaviour of zinc electroplating from alkaline cyanide-free electrolyte

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Two similar polymeric organic compounds from the polyquaternium family were studied as levelling additives in an alkaline cyanide-free zinc plating electrolyte. One additive (LA) has amide bonds between its monomers and the other (LU) has urea unions in its chemical structure. Copper cementation on zinc and gas evolution during aging of the zinc coatings were used to evaluate the effect of the chemical structure of the organic additives on the characteristic deleterious aging process of the coatings when electrodeposited with LA. Scanning electron microscopy and X-ray diffraction were used to follow surface morphology and crystallographic modifications of the coatings during aging. Faster copper cementation kinetics, zinc whiskers growth, blistering of the coating and N_2, CH_4, CO_2 and H_2 evolution were observed during accelerated aging of the coatings when LA was used. The coatings produced with LU did not show any aging effect. These studies show the strong influence that subtle changes in the chemical structure of the organic additive may have on the performance of zinc coating during storage.

Keywords: Electroplating, Zinc, Cyanide-free electrolyte, Alkaline, Organic additives

Introduction

Despite the well-known advantages that cyanide-free electrolytes represent from the environmental and human health point of view,[1] in order to achieve good quality coatings it is necessary to use additives with rather strong levelling and brightening power. These are generally organic compounds and can be classified according to their effect on the coating aspect and quality. For instance, levellers or carriers are compounds that, when added to the electrolyte, produce smooth deposits. According to the accepted theories,[2,3] the levellers are preferentially adsorbed on the protrusions of the cathode surface (peaks), blocking these sites and favouring the electrodeposition in the valleys of the metal surface topography. The most common levellers for zinc plating from alkaline non-cyanide baths, developed after 1940[4] are organic polymers, such as polyethylene glycol, polyvinyl alcohol and the especially effective polycationic polymers (polyquaternium family)[4–9] among others. Brighteners, usually aromatic or heterocyclic aldehydes,[4,5] make up a second group of organic additives, which act as grain refiners and, as a consequence, produce deposits with a microscopic roughness of the order of visible light wavelength and, therefore, they are able to reflect the incident light instead of dispersing it.[2]

The addition of organic additives to a plating bath implies the modification not only of the physical characteristics of the coatings but also their behaviour when exposed to the environment during use. It has been reported that the corrosion resistance, the mechanical properties and the crystal morphology of zinc deposits change depending on the additive interaction with the plating process.[4,10,11] Copper cementation reaction is normally used as a standard test in the electroplating industry to evaluate zinc coating homogeneity.[12] It is known that for some specific levellers zinc coatings suffer an aging process when stored, producing the acceleration of the copper cementation kinetics, showing anomalous results of the above mentioned test. In the present work, the influence in zinc coating aging of two similar organic polymeric compounds from the polyquaternium family, generally used as levellers in alkaline zinc electroplating was studied. The main difference between these additives is the chemical union between their monomers in the polymeric structure. One leveller has amide bonds (LA) while the other presents urea unions (LU). Strong evidence was found that subtle changes in the chemical

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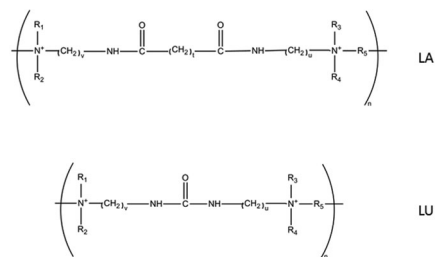
1 General formula of the additives used in this work. R_1 to R_4 can be $-CH_3$, $-CH_2CH_3$, $-CH$, $-(CH_3)_2$, $-CH_2CH_2OH$. R_5 can be $-(CH_2)_n$ with $n = 2–4$, $-CH_2CHOHCH_2$, $-CH_2CH_2O$ CH_2CH_2

structure of organic additives produce noticeable modifications in coating performances. This fact provides new elements for additives design in the electroplating industry.

Experimental

Zinc electrodeposition and coating aging

A standard electrolyte for zinc electrodeposition (S) with 0.45 M of ZnO was prepared using double-distilled water. NaOH (99%) was added in order to adjust the NaOH/ZnO ratio (R) to 7.

Two levellers, LA and LU, were tested. Both additives are polymeric quaternary amines, widely used in zinc electroplating in alkaline media[6] with the general formulae shown in Fig. 1, one with amide bonds between monomers and the other with urea unions. Both compounds were added to the electrolyte in a concentration of 25 mL L^{-1}. A brightener (B) was added in a concentration of 1 mL L^{-1}.

Zinc deposits were obtained on 17 mm-diameter rotating cylinders made of SAE 1010 steel bars at a current density (CD) of 4.3 A dm^{-2} during 13 min (coating thickness ~15 μm as the cathodic efficiency, determined by weight measurements, was approaching 100%) with a rotation speed set at 80 ± 5 rev/min^{-1}. The bath temperature was 50°C.

To accelerate the aging process of the coatings, the coated cylinders were heated in a conventional oven at 200°C for different times. This method reduced from months to hours the time in which aging effects show up. All the samples produced during the present study are listed in Table 1.

The brightener had an effect on neither the appearance nor on the aging phenomena when used with LU and consequently, will not be taken into further consideration.

Additionally, the samples were characterised with a SEM Quanta200 FEI microscope (Tungsten filament source) equipped with an EDS detector.

Copper cementation reaction

A supersaturated (36% w/w) $CuSO_4 \cdot 5H_2O$ solution in double-distilled water was neutralised by the addition of 0.80 g L^{-1} of CuO and filtered after 48 h according to ASTM.[12] Zinc coatings were evaluated counting the number (NI) of one-minute immersions in the above-described solution at 18°C until fully cemented metallic copper appears on the cylinder surface. The

Table 1 Zinc deposits obtained with different plating baths

Sample identification	Plating bath	Length of the TT/min
S-0	S	0
S-120	S	120
LA-0	S + LA + B	0
LA-8	S + LA + B	8
LA-17	S + LA + B	17
LA-34	S + LA + B	34
LA-51	S + LA + B	51
LA-68	S + LA + B	68
LA-85	S + LA + B	85
LA-102	S + LA + B	102
LA-120	S + LA + B	120
LU-0	S + LU	0
LU-8	S + LU	8
LU-17	S + LU	17
LU-34	S + LU	34
LU-51	S + LU	51
LU-68	S + LU	68
LU-85	S + LU	85
LU-102	S + LU	102
LU-120	S + LU	120
LUB-0	S + LU + B	0
LUB-120	S + LU + B	120

electrochemical potential of the surface of the cylinders was registered during the immersion tests using a Pros-kit® MT-1860 digital multimeter and its data acquisition software. A saturated calomel electrode was used as reference electrode.

Gas chromatography

Zinc plated cylinders heated during different times (0, 8, 17, 34, 51, 68, 85, 102 and 120 min) were cut into small pieces (4 mm^2) and were introduced in a stainless steel reactor. An argon flow of 150 cm^3 min^{-1} was passed through the reactor for 2 h in order to ensure an inert-atmosphere inside it. The reactor was then closed and kept at 250°C for 2 h. The gases in the reactor after that process were analysed by gas chromatography (GC), using a TCD detector and a HAYESEP DB 100/120 packed column, in order to quantify the gases released by each sample.

X-rays diffraction and internal stress measurements

XRD analyses of the coatings were performed with a Philips 3020 goniometer and a PW 3710 controller with CuK_α radiation ($\lambda = 1.54$ Å) (nickel filter). Planar samples of zinc deposits were obtained by cutting pieces of the cylinders and flattening them. The influence of LU, LA and heating time on crystallite size (CS) and preferred crystalline orientation was determined by means of FullProof Suite software.[13] The texture coefficient (TC) was calculated using equation (1):

$$TC(\%) = 100 \cdot \frac{I_{hkl}/I^0_{hkl}}{(1/N) \cdot \sum (I_{hkl}/I^0_{hkl})} \quad (1)$$

where $I(hkl)$ and $I^0(hkl)$ are the diffracted intensity of the (h,k,l) crystal plane of the zinc deposit and of zinc powder with no preferred orientation used as reference, respectively, and N is the total number of reflexion planes considered in the analysis.[14]

The CS effects within FullProf are determined describing both instrumental and sample intrinsic profile by a
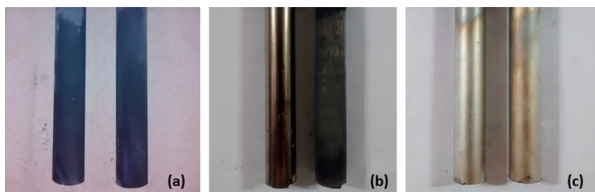
2 Zinc coatings produced with *a* S *b* S + LA + B and *c* S + LU before and after 120 min of accelerated aging at 200°C

convolution of Lorentzian and Gaussian components by means of the TCH pseudo-Voigt profile function.[15] The integral breadth method to obtain volume averages of sizes was used. The reported CS were calculated without considering anisotropy so they are only useful as comparative values.

Deposition with both additives was carried out on steel springs whose elastic constant (k/N m^{-1}) was measured utilising a series of calibration weights. The internal stress of the coating (S/N m^{-2}) was calculated considering the separation of the spring from its equilibrium position (Δx/m) and the section of the wire (A/m^2) using equation (2):

$$S = \frac{k \cdot \Delta x}{A} \qquad (2)$$

Results and discussion
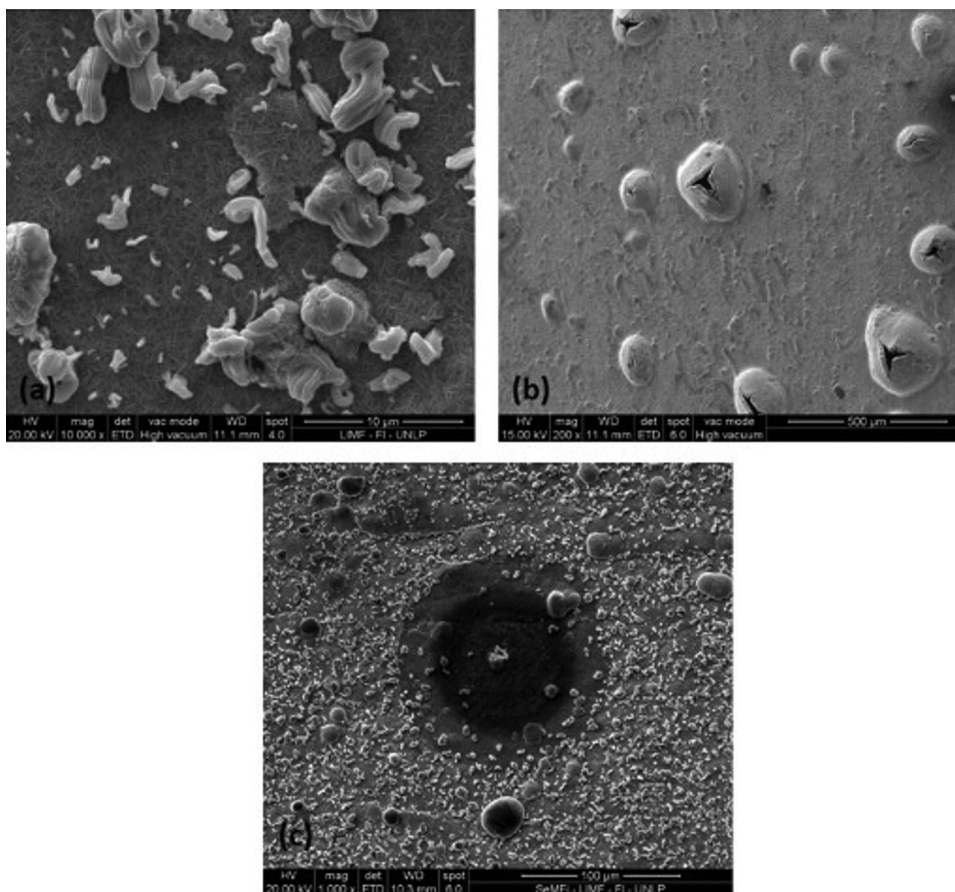### Zinc deposits and accelerated aging

The samples S-0 and S-120 were rough, opaque and presented a dark grey colouration, whereas zinc deposits LA-t and LU-t were smooth and bright.

After 120 min of heating, the colour and brightness of S-120 and LA-120 was considerably different, while LU-120 remained almost the same (Fig. 2).

SEM images of the coatings at 2500× magnification are shown in Fig. 3. The coatings produced without additives differed considerably from those obtained with them, having globular, uneven morphology. The sample LA-0 showed a needle-like crystalline structure, which can be clearly seen in the zoom detail in Fig. 3c, taken at 10 000× magnification. During heating, even at short times, it presented several changes. First, the presence of zinc whiskers from $t = 8$ min onwards, and second, the cracking of the coating. Whisker growth is a problem usually associated with the relief of internal stresses of the metallic coating and is commonly found in zinc and tin devices, presenting serious difficulties in the electronic industry since they can provoke short circuits.[16] For the case of tin, it has been reported that the microstructure of the deposit could induce whisker growth.[17] In the case of LA deposits, whiskers grew from beneath the zinc needles and from the edges of the cracks that appeared after 1 h of heating (Figs. 4 and 5). In order to discard the generation of blisters as a consequence of
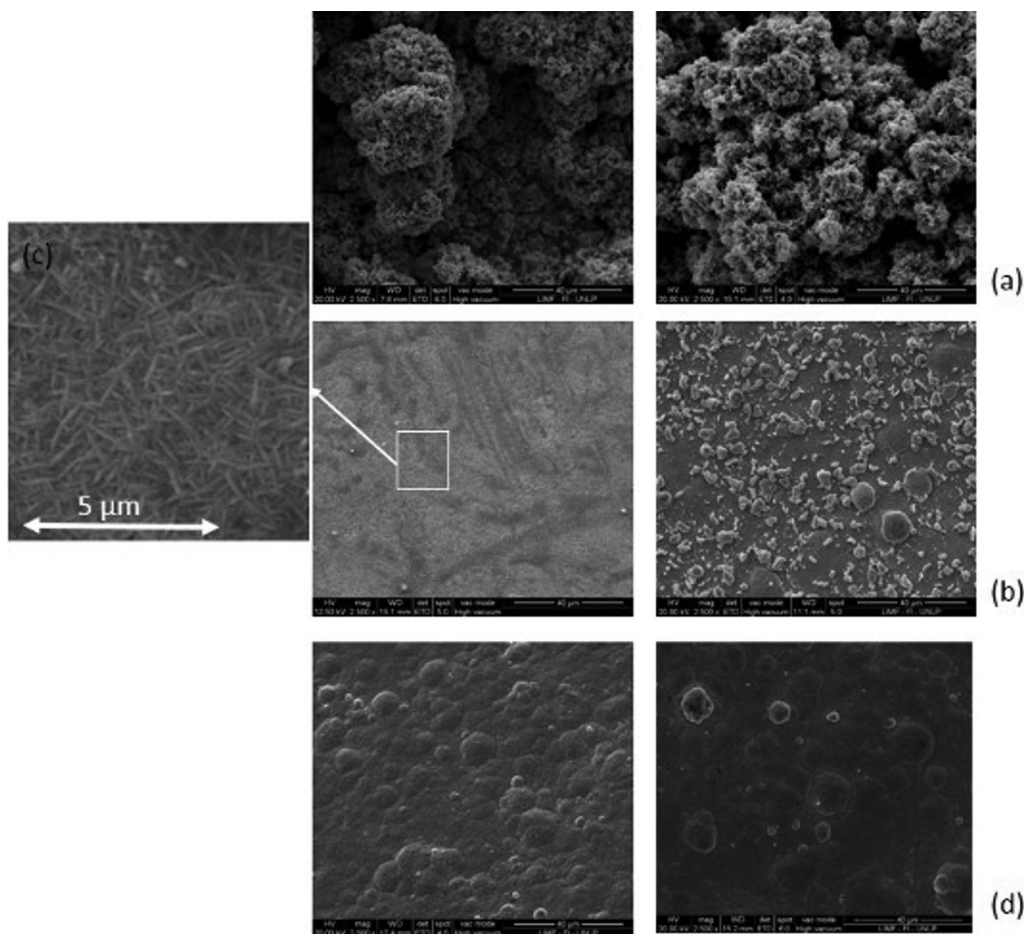
3 SEM images of the zinc coatings obtained with *a* S (2500×), *b* S + LA + B (2500×), *c* S + LA + B (10 000×) and *d* S + LU (2500×) before and after 120 min of accelerated aging at 200°C

4 **SEM images of *a* whiskers (scale bar 50 μm), *b* blisters (scale bar 500 μm) and *c* uncovered blister (scale bar 100 μm) observed in the zinc deposit from S + LA + B after 8 and 68 min of accelerated aging at 200°C, respectively**

poor adherence of the coating to the substrate, the top of some cracked blisters was removed using a pair of tweezers with the aid of an optical microscope. The bottom of the open blisters was analysed by SEM and EDS again and it was found that the substrate was still covered by zinc (Fig. 4*c*). This evidence suggests that the blisters build up during the release of gases trapped or generated between inner layers of zinc coating. Based on the chemical nature of the simple gases evolved during baking, it is possible to assert that the organic molecules that constitute the additives used in the plating bath are adsorbed during electrodeposition and decomposed by the heat treatment. This will be further discussed in the section 'Gas chromatography'.

On the contrary, LU generated a globular zinc deposit, which did not change significantly after thermal treatment of any length. For the case of LU, the presence of blisters was not noticeable in the deposit even after the coating was kept at 200°C for 2 h.

Copper cementation reaction

The dependence of NI with heating time is shown is shown in Fig. 6. LA coatings had a NI of 3.8 before being treated. A decay of the NI was observed after
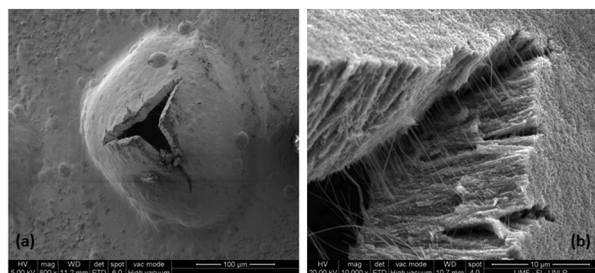
5 **SEM images *a* 800× (scale bar 100 μm) and *b* 10 000× (scale bar 10 μm) of the zinc deposit from S + LA + B after 68 min of accelerated aging showing the growth of zinc whiskers from the edges of the cracked blister**
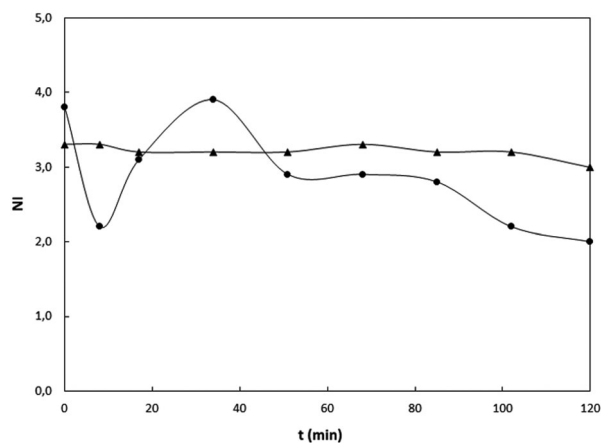
6 **Number of immersions resisted by the zinc coatings as a function of the aging process length for S + LA + B (dot) and S + LU (triangle)**
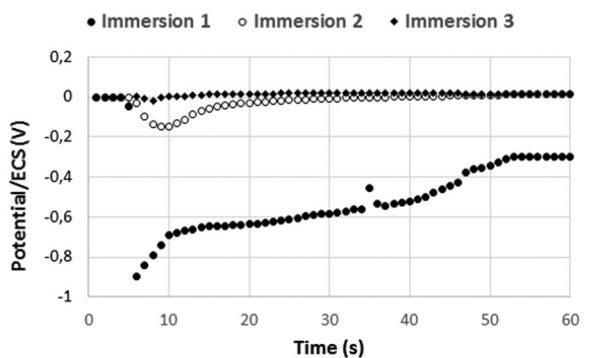
8 min at 200°C followed by a recovery to 3.9 for 34 min. For 120 min, NI diminished to 2. LU deposits showed a completely different behaviour as NI remained almost constant (between 3 and 3.2) during all the aging process durations.

The electrochemical potential of the surface of the coating as a function of time was registered for each immersion in order to study the copper cementation reaction onto the zinc coatings. When the potential shifted to the copper reduction potential, all the surface is covered with metallic copper and the test is considered finalised. With this improvement of the study, it was possible to measure fractions of NI. Table 2 shows the initial (E_i) and final (E_f) potential values for some of the samples and in Fig. 7 two of the potential vs. time curves are presented as examples.
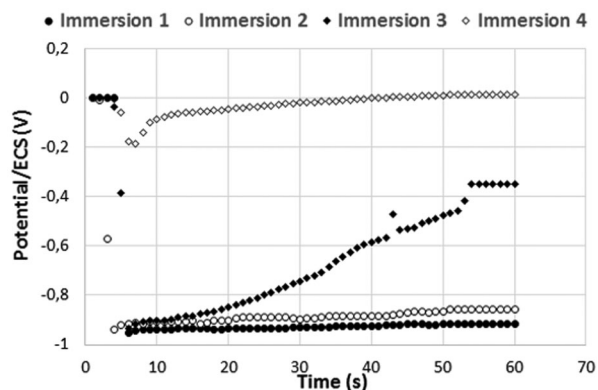
As expected all measurements ended at very similar E_f but the results show marked differences in E_i according to the additive used and the heating time. LA-t coatings for short heating times (LA-0 and LA-8) had E_i values
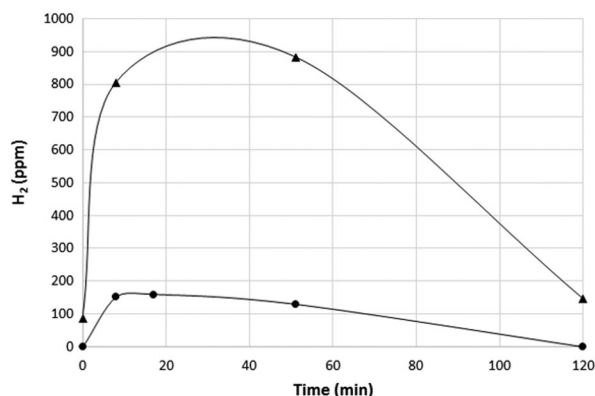
close to the equilibrium potential of zinc at this temperature and in this solution (-0.76 V/SHE), whereas for longer heating times (LA-51 and LA-85) E_i values were presented more similar to the equilibrium potential of iron (-0.44 V/SHE). In contrast, LU samples had E_i values similar to the zinc reduction potential for all the tested heating times. This behaviour is consistent with the structural modifications of LA-t coatings showed by the SEM images in the section 'Zinc deposits and accelerated aging'.
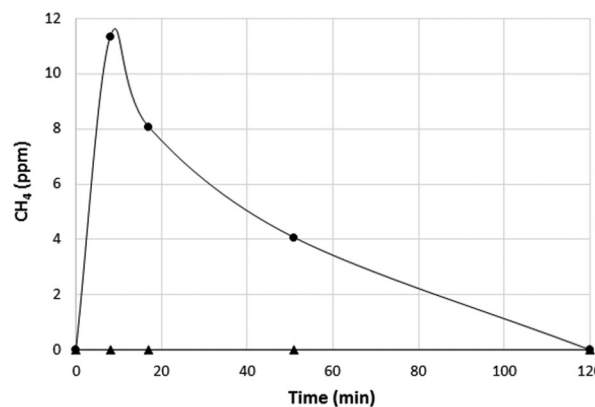
Gas chromatography

Four gases were released from the coatings heated in the sealed steel reactor and quantified by GC: hydrogen, nitrogen, carbon dioxide and methane. As can be seen in Figs. 8–11, the type and quantity of gases varied according to the additive used and the heating time during accelerated aging. The results are expressed in mg of gas per kg of coating.

For LA-0 and LU-0 only N_2 and CO_2 were detected. During heating LA samples released N_2 and CH_4, gases which did not appear in the reactor atmosphere for LU coatings. Also, LU samples evolved higher quantities of H_2 within the first hour of accelerated aging; afterwards it decreased reaching a value similar to the initial.

It seems that LA is incorporated in the zinc coating during electroplating and, later, its degradation during
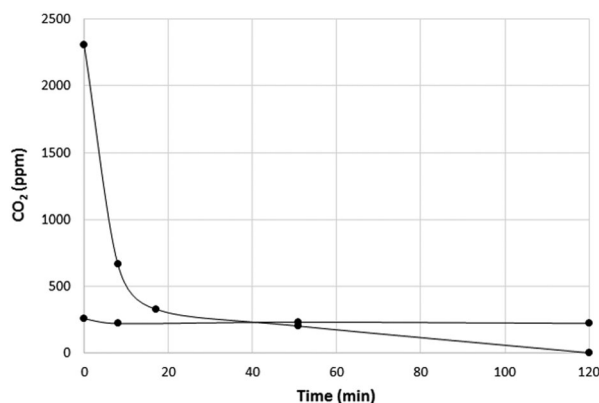
Table 2   Initial and final potentials of the system in copper cementation reaction

Sample identification	E_i vs. SHE/V	E_f vs. SHE/V
LA-0	−0.691	0.255
LA-8	−0.656	0.258
LA-51	*−0.372*	0.286
LA-85	*−0.320*	0.284
LU-0	−0.648	0.289
LU-8	−0.627	0.290
LU-51	−0.632	0.295
LU-85	−0.618	0.294

8 H_2 released from the zinc coatings obtained with S + LA + B (dot) and S + LU (triangle) after different times of aging at 200°C

7   Potential as a function of time for samples LA-0 and LA-8 in each immersion of the copper cementation test

9 CH_4 released from the zinc coatings obtained with S + LA + B (dot) and S + LU (triangle) after different times of aging at 200°C
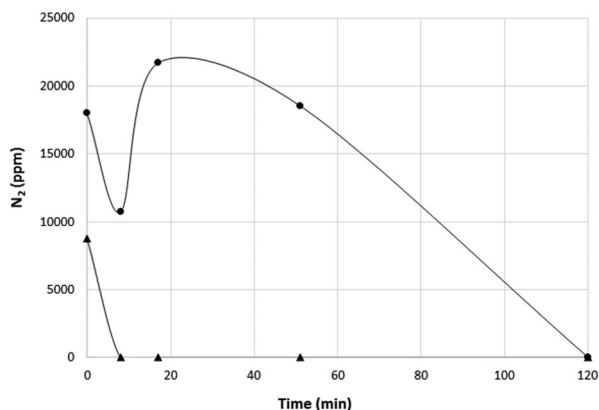
10 N_2 released from the zinc coatings obtained with S + LA + B (dot) and S + LU (triangle) after different times of aging at 200°C
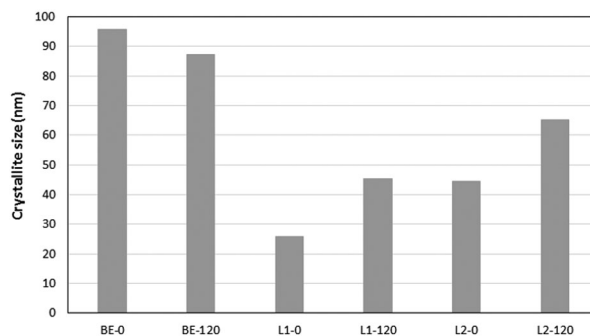

11 CO_2 released from the zinc coatings obtained with S + LA + B (dot) and S + LU (triangle) after different times of aging at 200°C

12 Dependence of the CS on the plating bath and the time of the accelerated aging process

13 TCs calculated for the zinc deposits from S (solid black), S + LA + B (horizontal stripes) and S + LU (dots) for *a* *t* = 0 and *b* *t* = 120 min of aging

aging releases gases through the deposit. As a consequence, it could be said that the aging process is related to the degradation of certain functional groups of the additive molecules and the release of gas would be detrimental for the performance of the zinc coatings in the copper cementation tests.
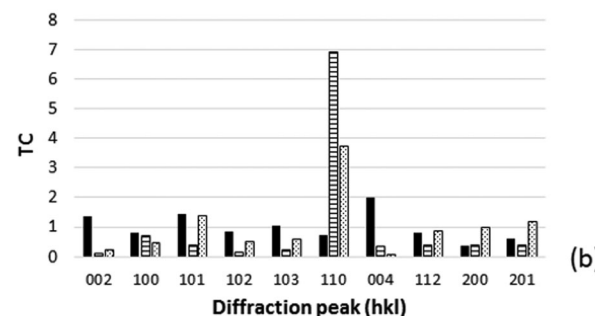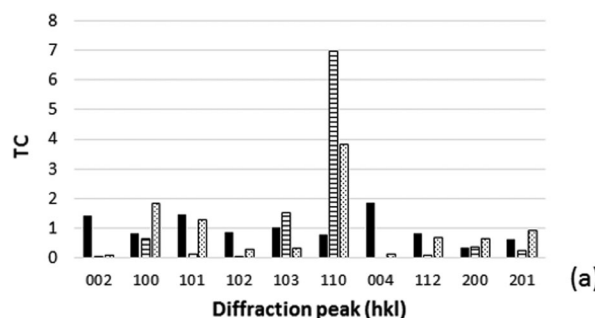
An alternative possible mechanism by which gases diffuse into the coatings which relies on the normally low cathode current efficiency (CCE) of alkaline cyanide-free electrolytes aiding significant hydrogen release at the cathode is not thought to be viable in this case. Such a concept would only explain hydrogen release, not the other gases, and preliminary determination of CCE in the particular bath tested by the authors showed that at the low NaOH/ZnO ratio used (~7), CCE was much higher at >90% than baths normally used which have significantly higher ratios, and lower CCE values.

X-ray diffraction and internal stress measurements

S, LA and LU samples were studied before and after 120 min of accelerated aging. In Fig. 12, it can be seen that the minimum CS is achieved using LA, followed by LU and finally by S. This result is consistent with the grain refining effect expected for organic additives. Although the CS decreased (9%) after the completion of the accelerated aging when no additives were employed, an increase in its value was observed with organic additives in the plating bath.

The TC was calculated using equation (1). When the coating was produced without leveller, no preferential orientation was observed whereas when LA or LU were added, the crystallites were oriented parallel to the plane (110) (Fig. 13). Despite the difference in brightness observed for the two additives, both deposits had the same crystallographic orientation. This fact agrees with the results reported by Nikolić *et al.*[18,19] A comparison of the TC for samples LA-t and LU-t (Fig. 14) proved that the effect of the length of the heating on the crystallographic orientation of the zinc coating was negligible with both LA and LU since the crystallites remained preferentially oriented parallel to the plane (110).

The elastic constant of the springs used in the internal stress determinations was $k = 103.9$ N m^{-1}. The spring coated from the S + LA + B bath presented higher Δx than the one plated with the S + LU bath. The internal stresses were 489 and 163 N m^{-2}, respectively, both of
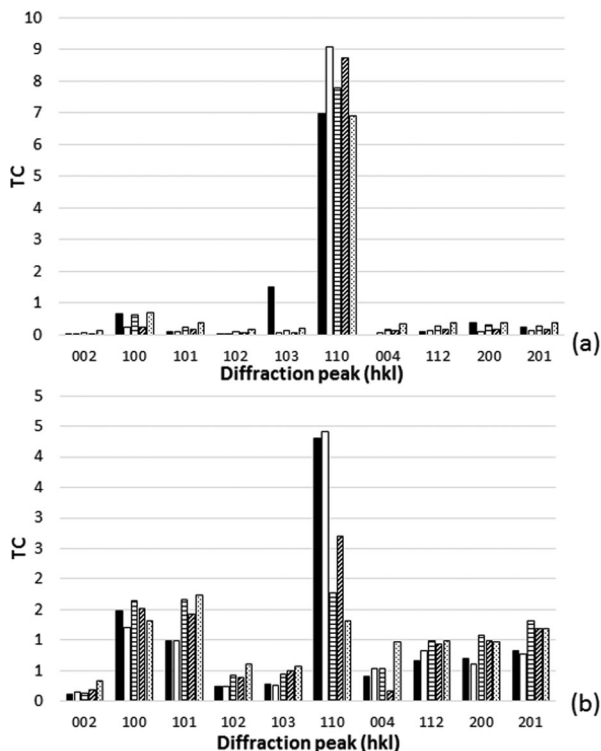
14 Comparison of the TC for *a* S + LA + B and *b* S + LU as a function of the aging time

compressive nature. The higher internal stresses developed with the S + LA + B bath could be related to the appearance of whiskers during accelerated aging.

Conclusions

Zinc deposits were obtained successfully from a cyanide-free plating bath containing different organic additives. The chemical characteristics of these additives had an effect on the morphology of the coatings as can be seen from the SEM images presented in this work.

Moreover, the nature of the addition agents modified the behaviour of the coatings subject to the studied aging process related to corrosion resistance. From the results of the copper cementation reaction experiments, it can be concluded that the system S + LA + B is more sensitive to the aging as the number of immersions until fully cemented metallic copper appears (NI) fluctuated for this combination, and was practically constant for S + LU when accelerated aging process was carried out.

The GC studies showed that according to the additive used, the gases released by the samples varied in composition and quantity. The main difference was noted for CH_4 and N_2. This result suggests that only one additive (LA) is incorporated in the coating and that its degradation products damage the deposit as they are released during the mentioned aging of the samples.

Even though the preferential orientation for the coatings of both systems was the same, a significant difference in their appearance could be noticed. This conclusion is consistent with the results reported by Nikolić *et al.*[18,19] for copper and zinc electrodeposits.

The use of LA favoured the growth of zinc whiskers when the cylinders were aged. This fact is detrimental to the industrial application of these coatings and therefore, a disadvantage for this additive formulation. No whiskers were observed with the use of LU.

According to the results obtained, the plating bath containing LU (with urea bonding) appears to be the most suitable system for zinc plating in alkaline cyanide-free media.

Acknowledgements

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