

the electrodeposition of zinc on mild steel in acid-chloride solution

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AN INVESTIGATION has been made using scanning-electron microscopy into the effects on the surface effects of some organic additives during the electrodeposition of zinc on mild steel in acid-chloride solution. The organic additives thiourea, dextrin and glycine were used in different combinations with the acid-chloride solution. The ultrasonically-cleaned steel surface was analysed by ESCA instrumentation before the electrodeposition process, which was carried out using a DC supply within defined operating parameters. The results obtained indicated a good electrodeposition of zinc on mild steel.

Introduction

The toxicity of cyanide-based baths and costly effluent-disposal which results from the stringent regulations against water pollution, in addition to the need to prevent corrosion and to enhance the aesthetic value of steel components in various industries and in domestic use, has led to increased interest in, and accelerated growth of, acid-zinc based baths in recent years.

However, while research has been continuing into improving the alkaline- and acid-sulphate baths[1-5], with particular attention to the effect of additives, very little or no attention has been given recently to the acid-chloride bath in this respect. The reason for this could be related to the development of commercial proprietary additives [6-9] for bright zinc electrodeposition on steel.

Apart from the research interest, the need to develop other non-proprietary additives for the acid-chloride bath is one of the objects of the present investigation. The thiourea, dextrin and glycine used here have been previously used as effective organic additives in acid-sulphate baths[10-14]. This work therefore investigates, using scanning electron-microscopy, the effects of these organic additives on the electrodeposition of zinc on mild steel in acid-chloride solution. The deposition is expected to provide good corrosion protection and to be of considerable technological and economic importance.

Experimental procedure

Preparation of test specimens

A Swedish-made mild steel, SIS 14147, which has a nominal composition of 0.038%C, 0.19% Mn and the rest Fe, was used as the test specimen. The 1-cm thick flat steel plate was cut into several test specimens each 10cm long and 1cm wide. At one end of each specimen, a length of 1cm was marked off for insertion into a plating solution for the electrodeposition of zinc.

The test specimens were degreased with *Henkel KR 6362-1*, a commercial alkaline degreasing chemical. The degreasing solution, prepared by dissolving 30g of the chemical in one litre of distilled water, was heated to a temperature of 65°C. The test specimens were fully immersed in the solution in the glass container and ultrasonically cleaned for 5min. The specimens were then removed from the degreasing solution, rinsed in distilled water, immersed in methanol and then immediately removed and air-dried. After drying, each specimen was then etched for 50sec in 3M HCl, rinsed in distilled water, immersed in methanol, again air-dried, and stored in a desiccator for further electrodeposition.

Preparation of electroplating solution and additives

The acid solution for electrodeposition consists basically of ZnCl₂ (71g/li), KCl (207g/li), and H₃BO₃ (35g/li). These were weighed, and five different 1-li

flasks were prepared, each containing the same chemicals in the same weights. Four of the flasks later received additives; the fifth flask was used without any additive.

The additives were: thiourea (0.75g/li), dextrin (3g/li), and glycine (2.5g/li). Each of these was weighed and prepared in four different combinations as follows: acid-chloride solution plus thiourea and dextrin; acid-chloride solution plus thiourea and dextrin and glycine; acid-chloride solution plus glycine and dextrin; acid-chloride solution plus glycine and thiourea.

Half-way through introducing the additives into four of the flasks, distilled water was also added and shaken to dissolve the chemicals. All five flasks, including the one without additives, were then filled with distilled water up to the 1-li mark.

A further three 1-li flasks were prepared, each receiving only one additive to the original electroplating solution: thiourea (0.75g/li) only was added to flask-1; dextrin (3g/li) to flask 2; and glycine (2.5g/li) to flask 3. All the contents of the flasks were dissolved in distilled water, and each flask was made up to the 1-li mark.

The flasks with the solutions were kept for further electrodeposition.

ESCA analysis of the steel surface

To determine its surface-film composition before immersion in acid-zinc plating solution, a 5 x 8-mm portion of the alkaline, degreased, and HCl-etched steel test-specimen was cut. This was put in an ESCA HP 59584 and the surface was analysed using x-ray photoelectron spectroscopy (XPS). Further sputtering of the film to a depth of 3Å (0.3nm) by Ar⁺ ion etching was made on the film for an in-depth study of the steel's surface-film composition.

Electrodeposition of zinc on steel

A 250-ml beaker was used as the plating container (bath), as shown in Fig.1. A perspex cover was prepared for the beaker by making a rectangular hole in the centre, two further rectangular holes equidistant from it, and a fourth round hole. The steel specimen was partially immersed in the plating solution (to a depth of 20mm) through the centre hole; similarly, two zinc specimens were partially immersed into the solution through the other two rectangular holes. The round hole was for a thermometer which was inserted in the solution to measure the bath temperature.

The steel specimen was connected to the negative side of a DC supplier, while the zinc specimens (also wired to each other) were connected to the positive side.

Each of the plating solutions was put into the beaker (bath) in turns. The pH was measured with

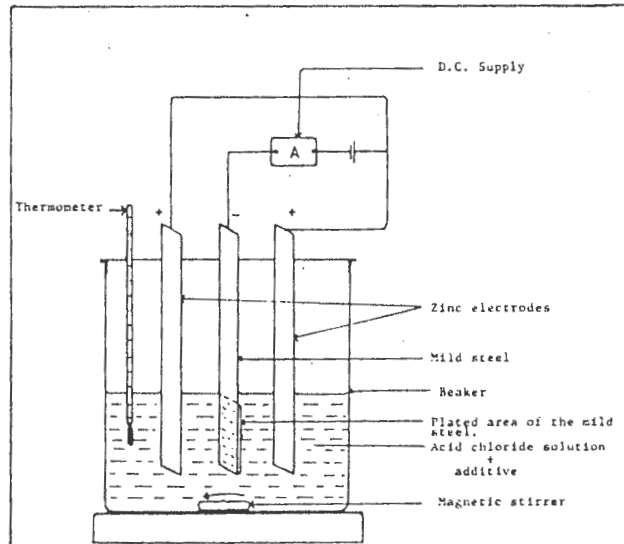


Fig.1. The experimental set-up.

a pH-meter and adjusted with zinc carbonate hydroxide to pH5. The other operating conditions were: temperature, 27-30°C; current, 30mA/sqcm; plating time, 30min; gentle stirring.

After each plating, the specimen was taken out, rinsed in distilled water, immersed in methanol, and quickly air-dried. The specimens were stored in a desiccator.

SEM characterization

A scanning electron-microscope (SEM) was used to examine the surface of each of the plated test-specimens, a small portion of each of which was cut and mounted on a stub. The specimens were examined in turn in the SEM, and electron micrographs were made of the representative areas of the surface at three levels of magnification: low (x40), medium (x480), and high (x1000).

Results and discussion

ESCA spectra

ESCA spectra recorded from the surface of the degreased steel specimen before electrodeposition are presented in Fig.2. Oxygen, iron, chloride and carbon were detected on the surface film. The signals for these respective elements show that oxygen and iron each produced two different peaks. The two peaks from oxygen represent oxide, O²⁻, and hydroxide, OH⁻, formed on the surface. The two peaks from iron represent a predominance of Fe⁺³, with Fe²⁺ also present. There is no change in the chloride, which comes mostly from the HCl which was used to etch the metal specimen. The carbon element must have originated from the methanol used to rinse the specimen before air drying.

Further sputtering of the surface film by Ar⁺ to an etching depth of 3Å indicates that OH⁻ is only

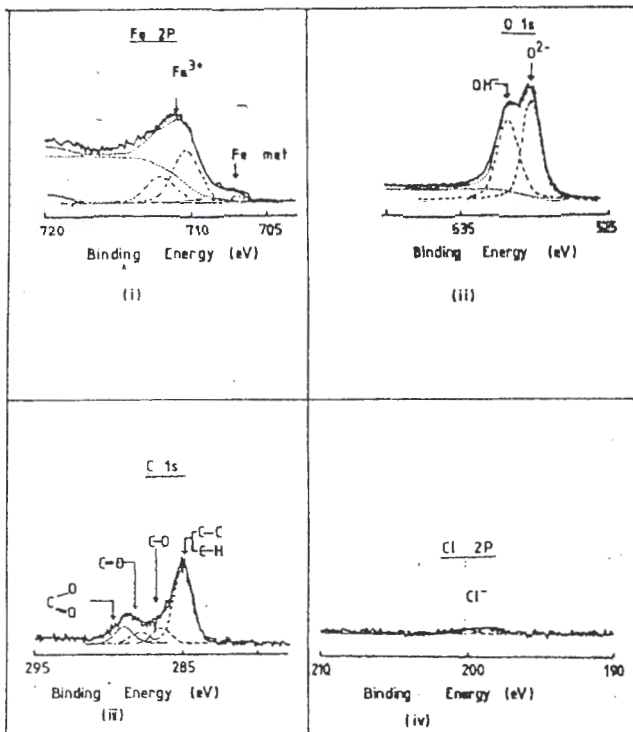


Fig.2. ESCA spectra recorded from the surface of the degraded and etched mild-steel specimen.

present on the surface. There was a chemical shift in which the OH^- signal almost disappeared. The peaks representing carbon and chloride were still obtained, but the signals were of very low intensity. The source of a low-intensity signal for sulphur obtained after ion-etching is not clear. Since the plating medium is sufficiently acidic to destroy the surface film of the metal specimen, it is not expected that the surface-film composition would have an adverse effect on the zinc-electrodeposition process.

Electrodeposition of zinc in acid solution only

The SEM micrograph of the surface of the mild-steel test sample before zinc electrodeposition is presented in Fig.3. Electrodeposition of zinc on mild-steel test samples from acid-chloride solution without any additive gave a deposition that was porous in some parts (Fig.4). At the higher magnification of x480, the structure shows big crystals that are closely packed, though pores are present. At a magnification of x1000, it is apparent that the crystals are coarse and separated, showing gaps or pores, and the surface is not smooth. This indicates that zinc-electroplating of metals in acid solution without any additives may not give wholly-effective protection, due to porosity.

Effects and characteristics of the additives

Addition of thiourea and dextrin to the basic acid-chloride solution gives an entirely-different surface structure, as shown in Fig.5. Visually, the



Fig.3. SEM micrograph of the etched surface of the mild steel test sample before zinc electrodeposition.

surface looks semi-bright. The scanning electron micrograph (Fig.5b) shows that the electrodeposited surface was smoother and denser than that resulting from the basic solution alone. It could also be seen clearly that the levelling effect of the additives resulted in an absence of surface porosity. At the low SEM magnification (x40) and higher magnifications (x480) and (x1000), the surface remained smooth in the sense that not a single trace of electrodeposited grain crystals could be seen and there was no particular defined grained structure on the surface. The mechanism for this levelling effect is not yet clear.

The SEM micrograph (Fig.6) for the addition of thiourea, dextrin and glycine to the acid-chloride solution, show structures that are quite different from those of thiourea and dextrin only. The effect of glycine is apparent. At low magnification (x40), Fig.6a, the surface structure resembles that of Fig.5a. At higher magnifications (x480 and x1000), the difference in structure is clear. While some of the levelling effect obtained by the addition of thiourea and dextrin only was observed again, the structure has been broken up, with some underlying finer grains of zinc deposition. It thus appears that glycine has the effect of producing crystals but with defective levelling. At the same time, the imperfectly-levelled structure has some pores which render doubtful its protective effect against corrosion.

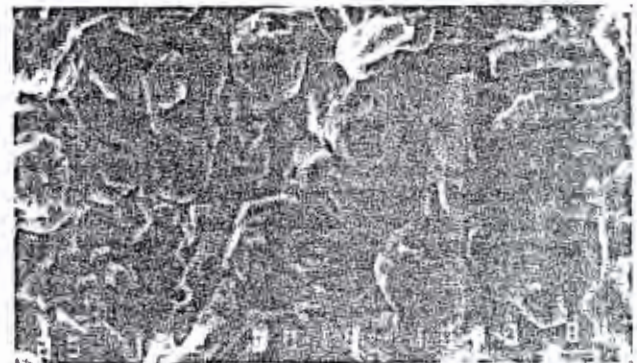
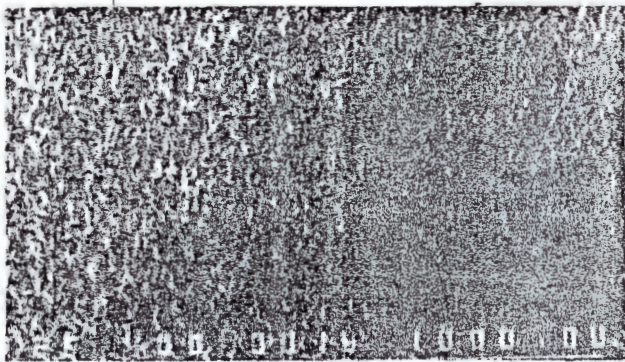


Fig.4. SEM micrograph of the steel surface after zinc electrodeposition in acid chloride solution without additive.
 (a) x 40 (above)
 (b) x 480 (above, right)
 (c) x 1000 (right)

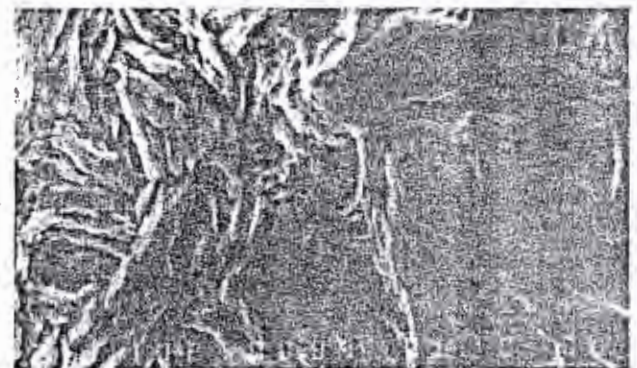
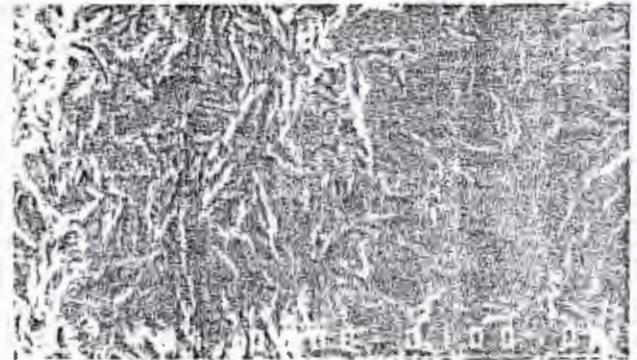
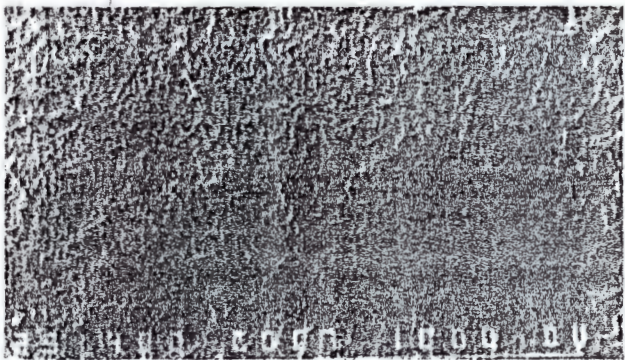


Fig.5. SEM micrographs showing the effect of thiourea and dextrin additives on the electrodeposition of zinc.
 (a) x 40 (above)
 (b) x 480 (above, right)
 (c) x 1000 (right)

The addition of glycin and dextrin to the acid-chloride solution also gives a deposition which is semi-bright to the visual observer. However, the scanning electron micrographs of the surface both at the low and higher magnifications as presented in Fig.7 show structures which are quite different at all magnifications from those previously discussed.

At the low magnifications, well-arranged crystals abound all over the surface while the picture beneath them is not clear. However at higher magnifications, it can be seen that underneath the crystals is a dense deposition of fine grains or crystals covering the whole surface. The phenomenon that led to the deposition of the

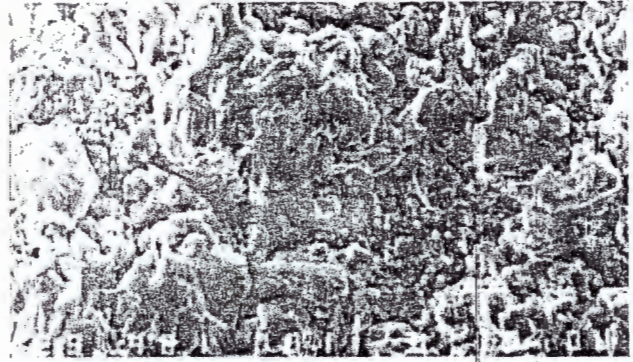
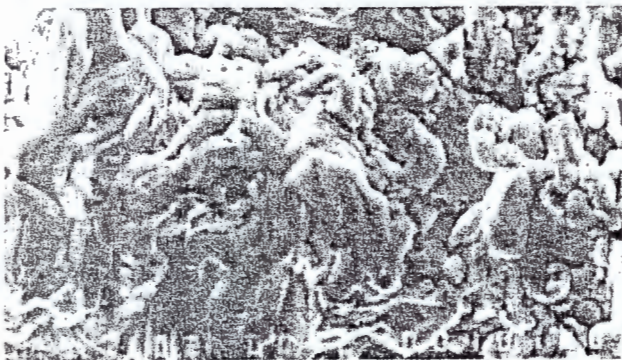
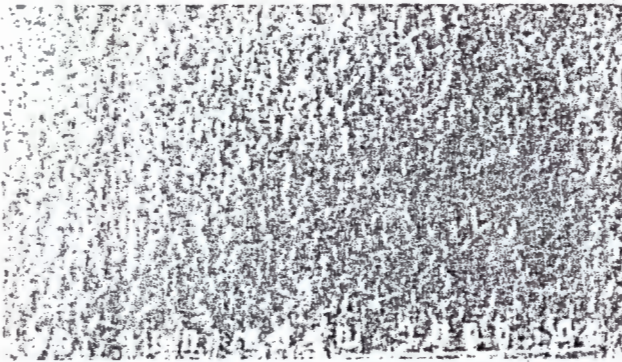


Fig.6. SEM micrographs showing the effect of thiourea, dextrin and glycin additives on the electrodeposition of zinc.

- (a) x 40 (above, left)
- (b) x 480 (above)
- (c) x 1000 (left)

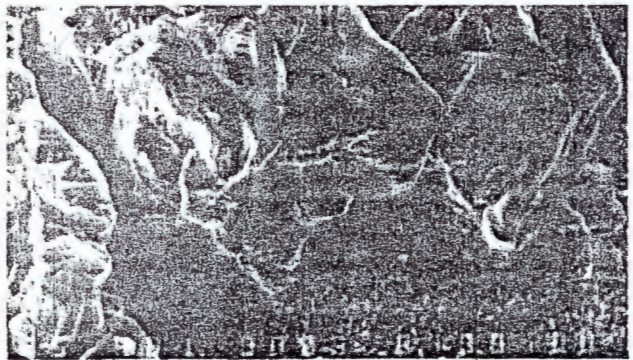


Fig.7. SEM micrographs showing the effect of glycine and dextrin additives on the electrodeposition of zinc.

- (a) x 40 (above, left)
- (b) x 480 (above)
- (c) x 1000 (left)

bigger surface crystals is not well understood.

However, it may be related to the prolonged plating time of 30min, which would have given rise to crystal growth.

Another different form of surface structure is obtained by the addition of thiourea and glycin to the acid-chloride solution as observed from the

SEM micrographs presented in Fig.8. At a magnification of x40, the structure obtained here looks very much like that obtained for the addition of glycine and dextrin. However, the crystals are wider and appear flat when compared with those obtained with the addition of glycine and dextrin.

The addition, in turns, to the acid-chloride

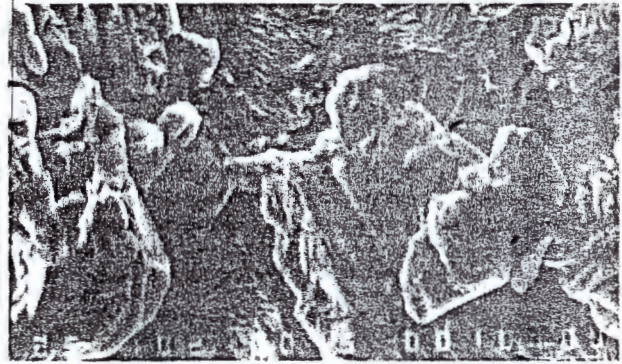
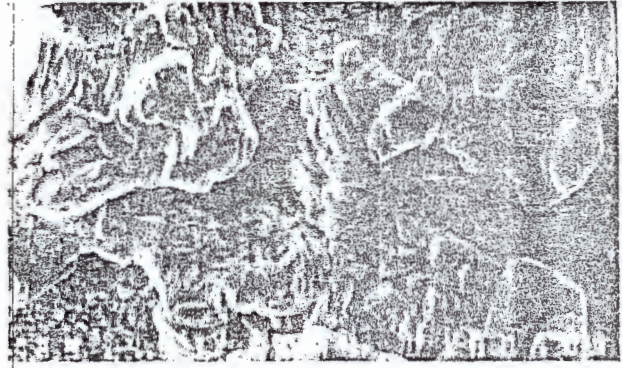
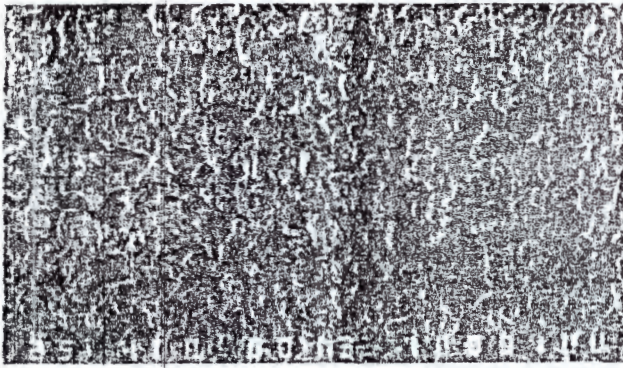


Fig. 8. SEM micrographs showing the effect of thiourea and glycine additives on the electrodeposition of zinc.
 (a) x 40 (above)
 (b) x 480 (above, right)
 (c) x 1000 (right)

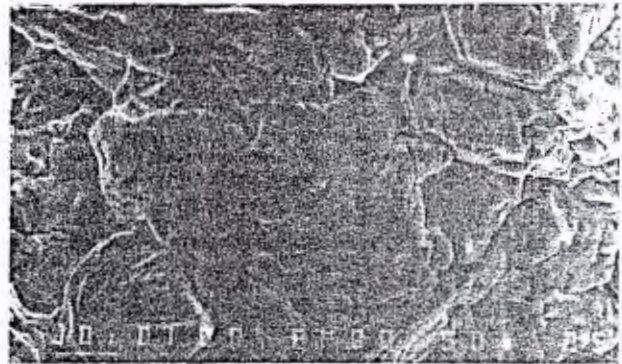
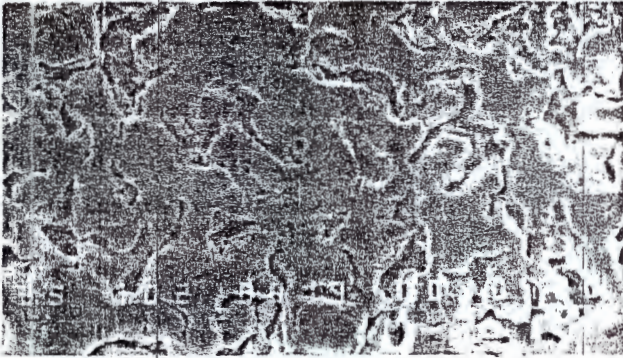


Fig. 9. SEM micrographs showing the separate effects of thiourea, glycine and dextrin addition in turn on the electrodeposition of zinc.
 (a) thiourea addition, x 1000 (above)
 (b) glycine addition, x 1000 (above, right)
 (c) dextrin addition, x 1000 (right)

solution of each of the additives separately used in this investigation (thiourea (0.75g/li), glycine (2.5g/li), and dextrin (3g/li)), produced good zinc electrodeposition on mild steel. This observation is apparent in the SEM micrographs (Figs 9a-c). It is clear, in general, that those additives did not reinforce one another in providing complementary

electrodeposition effects as an example of synergy. The structures obtained here are very different from those previously observed when the additives were used in different combinations, except for thiourea. The levelling effects of thiourea and the grain refinement of dextrin, as previously observed, were also very apparent here. Some small pores were

observed which indicate poor throwing power; additionally, the presence of the small pores could be due to the difficulty in controlling plating-bath parameters, particularly the pH and the plating temperature.

Conclusion

It is clear from the results obtained in this work that each additive behaves differently by imposing unique characteristics on the surface structure of zinc-electrodeposited steel. Glycin appears to be influencing the formation of bigger zinc grain-crystals on the zinc-electrodeposited surface, while dextrin influences finer grains on the surface. Thiourea appears more as a levelling agent that smooths the surface structure of the electrodeposited zinc; its tendency towards a brighter electrodeposited surface was apparent.

The plating period of 30min was quite long, and this could have enhanced the growth of surface crystals. The overall result indicates that the additives did not provide a synergistic or co-operative reinforcing effect. The additives studied provide good and characteristic surface structures, which although not comparable with the proprietary additives in terms of brightness and quality of surface structure, nevertheless offer good protection.

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