

The effect of additives on the electrodeposition of zinc on mild steel in acid chloride solution

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THE EFFECT of the addition of thiourea, dextrin and glycin, as organic additives, on the surface characteristics of zinc electrodeposition on mild steel in acid chloride solution at different pH levels and varying combinations of the additive, was studied in this investigation by SEM. The surface state, and hence the steel's surface-film composition, was analysed by ESCA instrumentation before zinc electrodeposition, which was performed using a DC supplier at defined operating conditions. The unique crystal structures obtained are characteristic of the different pH levels and different combinations of additives. The overall results show good zinc electrodeposition on mild steel, except for the porous effect of combined thiourea and glycin addition.

Introduction

The surface characterization of the effects of organic additives on the electrodeposition of zinc on mild steel and the influence of organic additives on the surface characteristics of zinc electrodeposition on mild steel in acid-chloride solution under different conditions have been demonstrated in recent works[1-2]. This article extends these investigations by further looking into the effect of thiourea, dextrin and glycin additions in different combinations and at two different pH levels for a constant plating time of 12.5min.

This work has been undertaken in an attempt to develop further other effective addition agents from organic additives for the acid chloride bath apart from the commercial proprietary additives[3-6] for bright zinc electrodeposition. Recent investigation performed on this subject has indicated the effectiveness of these additives. However, in order to obtain the optimum utilization of these additives, more work has to be done, and this is the object of the present investigation. The additives used in this work have been previously used in acid sulphate baths[7-11]

Results obtained from an investigation such as this could be beneficial in establishing other areas for the use of zinc-electroplated steel materials and/or products. It is expected that the zinc-electroplated products made from this acid bath using the additives under investigation will be commercially useful in corrosion protection of mild steel products; it will also be aesthetically beneficial. This work is expected to point the way to the use of other effective additives in acid chloride baths, particularly in fundamental research, since the composition of the additives are known.

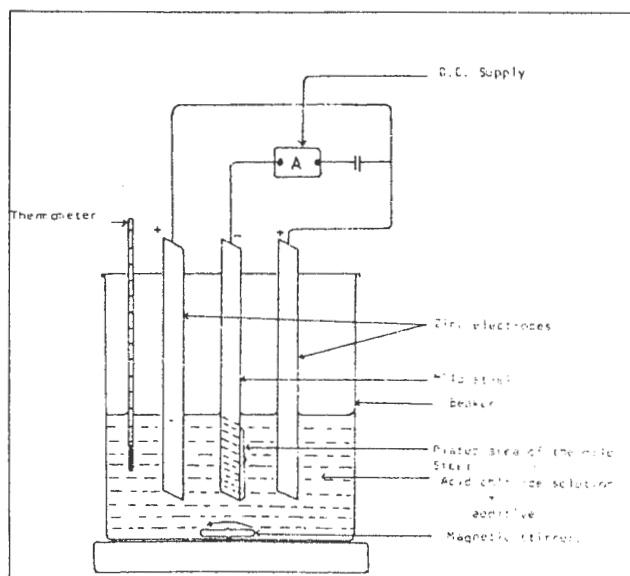
Experimental procedure

Preparation of test specimens and solutions

The experimental procedures used here, are described in the previous work[1,2]. A Swedish-made flat mild steel, SIS 141147, 0.1cm thick, with a nominal composition of 0.038%C, 0.19%Mn and the rest Fe, was cut into several test specimens of 10.0cm length and 1.0cm width. A portion 1.0cm in length was marked off at one end for the zinc electrodeposition.

Henkel VR 6362-1, a commercial alkaline degreasing-chemical, was used to degrease the test specimens. 30g of the chemical was dissolved in 1li of distilled water and heated to a temperature of 65°C. The test specimens were immersed in the

Fig.1. Schematic diagram of the experimental set up.



solution in a glass container and ultrasonically cleaned for 5min, then removed from the solution, rinsed in distilled water, immersed in methanol and then immediately removed and air dried.

The specimens were in turns etched for 50sec in 3M HCl, rinsed in distilled water, immersed in methanol, air dried, and stored in a desiccator.

The acid-chloride solution for the electro-deposition consisted of ZnCl (71g/li), KCl (207g/li) and H3BO3 (135g/li). Thiourea (0.75g/li), dextrin (3g/li), and glycine (2.5g/li) were used as the additives. Five flasks were prepared, four of the solution with additives and one without. The solutions from the group of four flasks were each then separated into two, with one portion having its pH adjusted with zinc carbonate hydroxide to pH5 from the original pH of 3.9 just before use.

ESCA analysis of the steel surface

Before immersion in acid-chloride solution, the surface-film composition, and hence the steel's surface, was determined, as this could affect the zinc-electrodeposition characteristics. A 5x8mm sample of the steel specimen (after degreasing and etching) was cut. This was surface analysed using X-ray photoelectron spectroscopy (XPS). The surface film was further sputtered by Ar⁺ ion etching to a depth of 0.3nm for an in-depth study of the steel's film composition. An unclean surface could have some adverse plating effects.

Electrodeposition of zinc on steel

The electrodeposition of zinc on the steel used in this work has been previously described[1,2]. Here, it was performed by partially immersing the steel specimen and the zinc electrodes in the 20-mm deep plating solution through the rectangular hole made on a prepared perspex cover for the 250ml-beaker used as the plating bath (Fig.1).

The steel specimen was connected to the negative side of a DC supply, while the zinc was connected to the positive side: the two zinc electrodes were also connected through a wire. The plating solutions were put, in turn, into the beaker (bath), and their respective pH was obtained by adjusting the original solution with zinc carbonate hydroxide.

The operating conditions were:

- pH of the solutions = 3.9 and 5
- temperature = 27-30°C
- current = 30mA/cm²
- plating time = 12.5min
- gentle stirring

After each zinc electrodeposition, the specimen was taken out, rinsed in distilled water, immersed in methanol and quickly air dried before characterizing the surface with the scanning electron microscope (SEM).

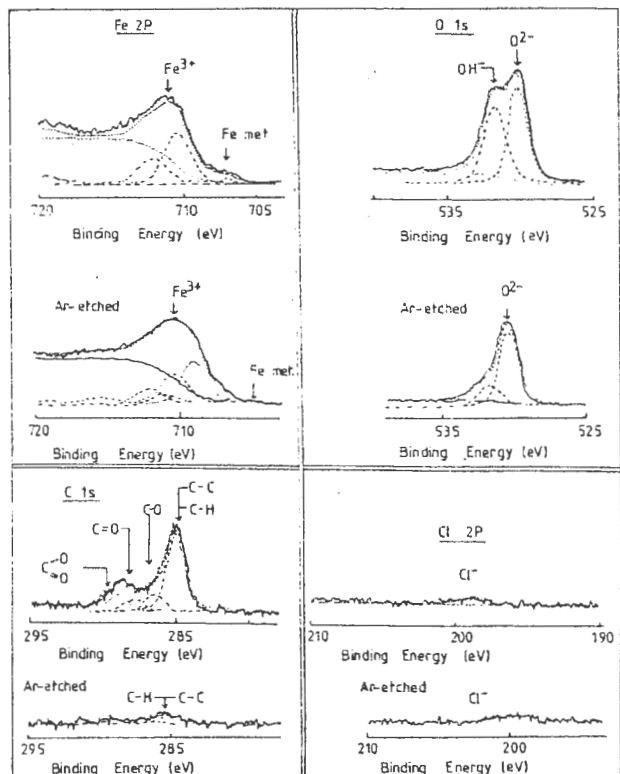


Fig.2. ESCA spectra recorded for the surface of the degreased and etched mild steel specimen.

SEM characterization

A small portion of each of the plated specimens was cut, mounted on a stub and examined in turn in the SEM. Electron micrographs were made of the representative areas of the surface at x100 and x1000 magnifications.

Results and discussion

ESCA spectra

The ultrasonically-cleaned steel surface film was analysed by ESCA instrumentation before the electrodeposition process, Fig.2. On the surface film oxygen, iron, chloride and carbon elements were detected. De-convolution of the signals for these elements was performed, giving two different peaks for oxygen and iron. The oxygen's two peaks represented oxide (O²⁻) and hydroxide (OH⁻) formed on the surface. The two peaks from the Fe signal represented Fe³⁺ and Fe²⁺. Chloride, which comes mostly from the HCl used to etch the metal specimen, shows no change. The traces of carbon are believed to have originated from the methanol used to rinse the specimen before air drying.

That OH⁻ was only present on the film's surface was indicated by further sputtering of the surface film by Ar⁺ to an etching depth of 0.3nm. There was a chemical shift, in which OH⁻ signal almost disappeared. The peaks representing carbon and chloride were obtained at very low intensity levels.

The plating medium was very acidic and could easily destroy the unstable surface film of metal

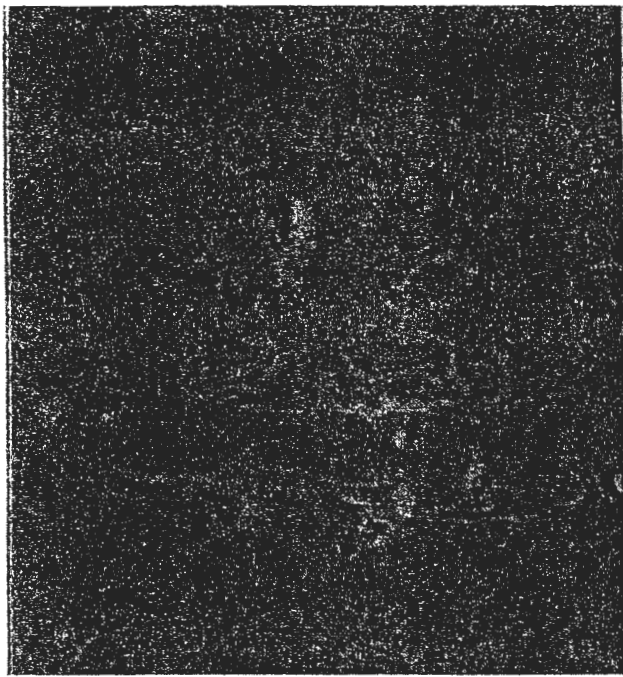


Fig.3. SEM micrograph of the etched surface of the mild steel test specimen before zinc electrodeposition.

specimen. There was no significant impurity obtained in the film. The steel's surface was therefore expected to serve as a good substrate for zinc electrodeposition, providing zinc plating with a minimum adverse effect, if any.

Electrodeposition of zinc in acid solution without additive

Fig.3 shows the SEM micrograph of the mild steel (test sample) surface before immersion in acid solution prior to zinc electrodeposition. No significant impurity was observed.

At a pH3.9 and plating time of 12.5min. the zinc-electrodeposited surface of the mild steel specimen (Fig.4(i-ii)) shows crystal structures that could be considered good. At a magnification of x100. Fig.4(i), no definite crystal structure could be discerned, although a very close observation indicates the presence of some pores. At a higher magnification of x1000. Fig.4(ii), a slightly coarse crystal structure is distinct, and very few tiny pores could be observed. The viability of this type of zinc plating will definitely depend on the conditions

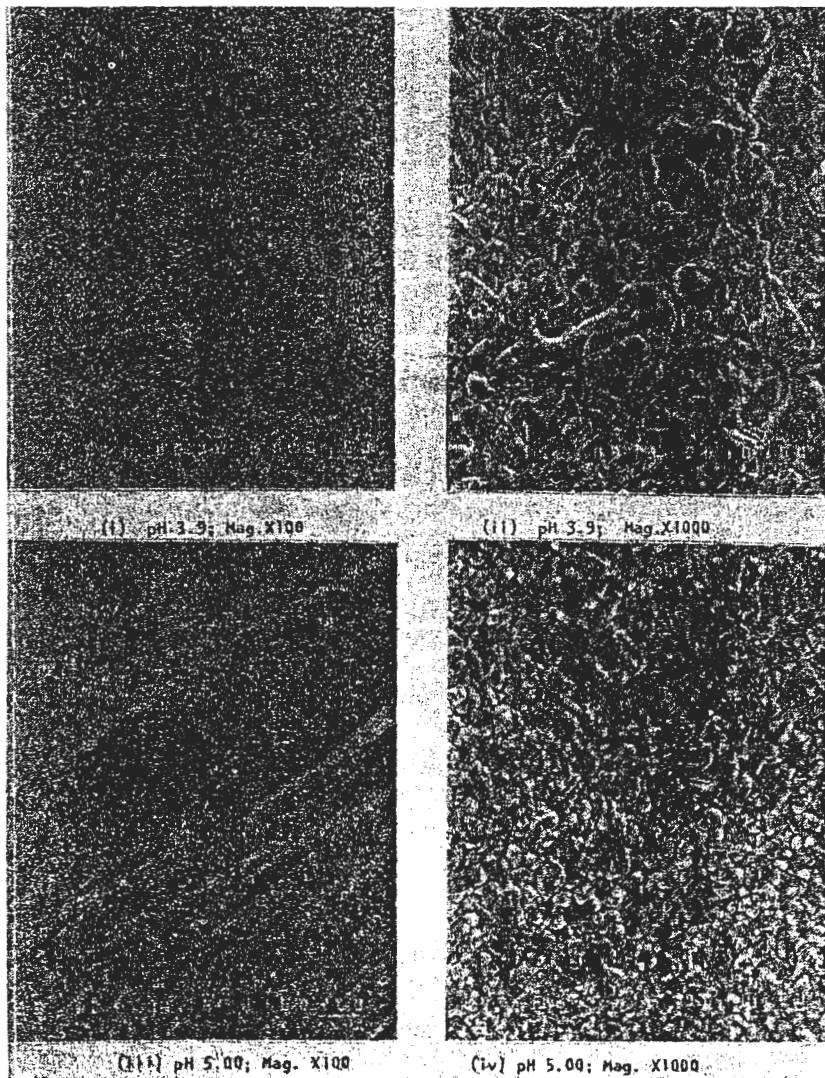
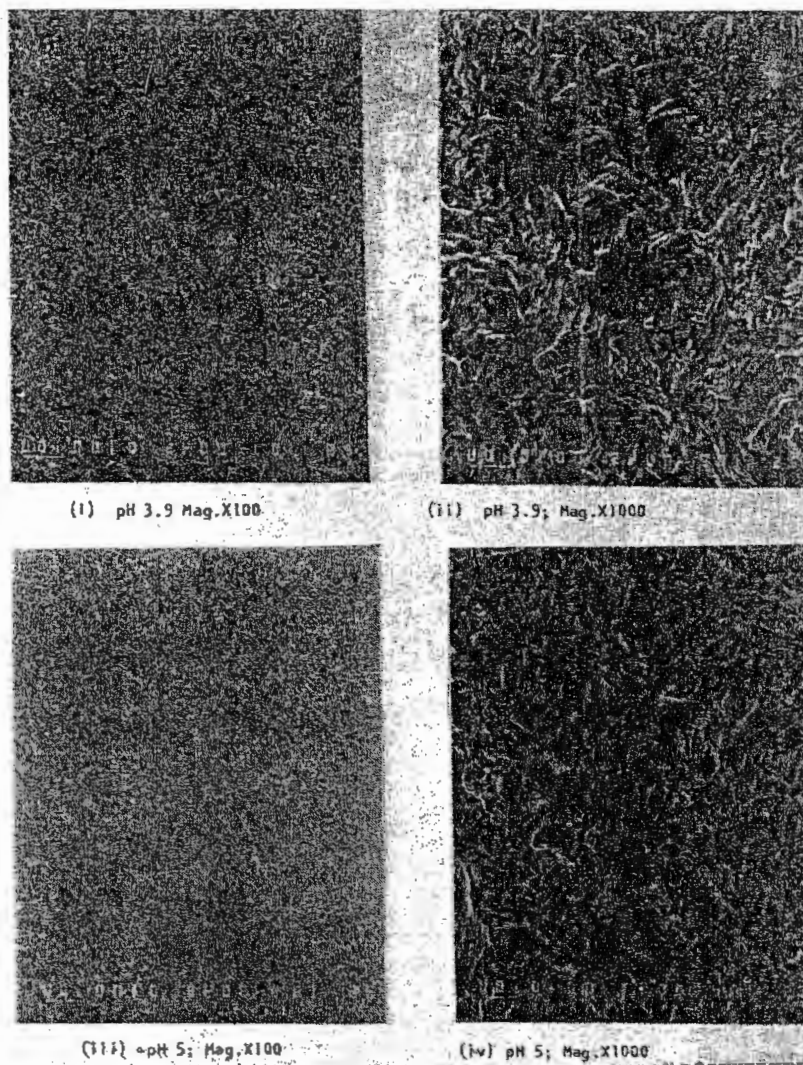


Fig.4. SEM micrographs of the steel surface after zinc electrodeposition in acid chloride solution without additive; plating time 12.5min.

Fig.5. SEM micrographs showing the effect of thiourea (0.75g/li) and dextrin (3g/li) on the electrodeposition of zinc on mild steel in acid chloride solution; plating time 12.5min.



under which it is applied. The poor throwing power of the acid solution, though not very apparent here, must have been responsible for the pores. The slightly coarse structure is due to the absence of levelling agents in the acid solution.

Fig.4(iii-iv) shows the surface structure of the zinc-plated steel at pH5. Fig.4(iii), at a magnification of x100, shows no defined structure, but an almost smooth surface. At a magnification of x1000, Fig.4(iv), the crystal structure is clear, and the crystals are more round and fine. This unique structure, which is evidence of good zinc-electrodeposition, arises from the addition of the zinc carbonate hydroxide that was used to adjust the pH from 3.9 to 5. The structure of Fig.4(iv) is actually due to a combination of factors - the pH resulting from zinc carbonate hydroxide addition, and hence the variation in the bath composition.

Addition of thiourea and dextrin

The addition of thiourea (0.75g/li) and dextrin (3g/li) to the acid solution at pH3.9 produces surface characteristics or structures, Fig.5(i-ii), which are different from those of Fig.4 in general.

Here the crystal structure is difficult to define. The surface looks like a unique weathered rock without any trace of pores, both at the low (x100) and at higher (x1000) magnifications. The addition of thiourea and dextrin has provided a levelling effect and also enhances better throwing power. The result indicates that good zinc electrodeposition on mild steel is obtained at this pH level and with the additives used.

Fig.5(iii-iv) shows the SEM micrograph obtained for the same bath but at different pH. At pH5, the structure obtained is slightly different from that obtained at pH3.9. The crystal structure here, though looking somewhat amorphous, is finer. The effect of this finer structure (if any) on the plating performance is theoretically difficult to say at present. It is apparent that the pH has a modifying effect through the addition of zinc carbonate hydroxide.

Addition of thiourea, dextrin and glycine

The addition of thiourea (0.75g/li), dextrin (3g/li) and glycine (2.5g/li) to the acid solution at pH3.9 and for a plating time of 12.5min produces a unique and

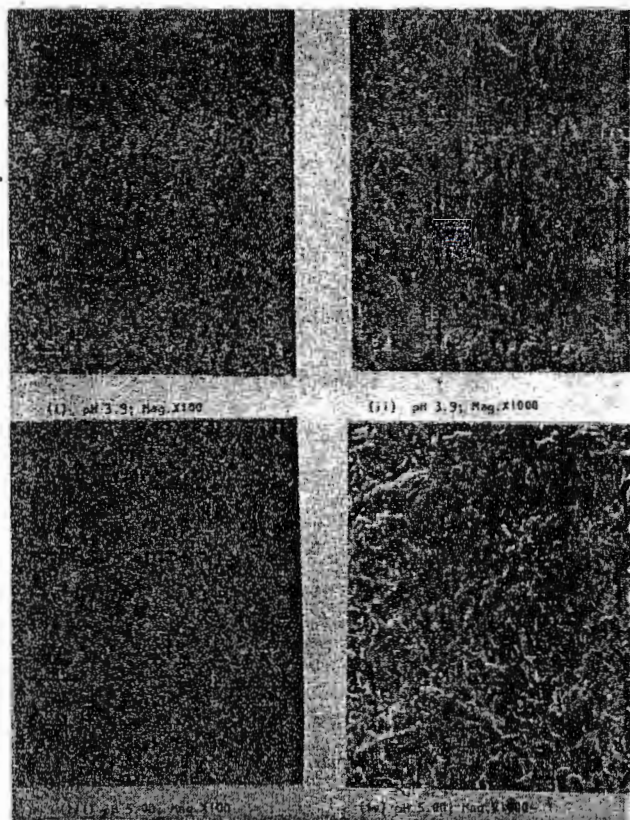


Fig.6. SEM micrographs showing the effect of thiourea (0.75g/l) and dextrin (3g/l) and glycine (2.5g/l) on the electrodeposition of zinc on mild steel in acid chloride solution; plating time 12.5min.

beautiful surface structure both at the low magnification of x100. Fig.6(i), and at high magnification, x1000 - Fig.6(ii). Fig. 6(ii) gives a clearer picture of the arrangement of the surface crystals which is difficult to describe. The surface structure indicates good zinc electrodeposition with an absence of surface pores. The surface structure obtained here looks different from that of Figs 5(ii) and 5(iv). This difference is apparently because of the difference in bath composition due to the further addition of glycine.

At pH5, after adjustment of the bath composition by zinc carbonate hydroxide, the surface structure of the electrodeposited zinc again looks different, Fig.6(iii-iv). Though still very compact and with no trace of any pore, the surface crystals, (Fig.6(iv)), are not as well defined as in Fig.6(ii). The technical effect of the difference on surface crystal arrangement or structure cannot be expressed at present. However, it is apparent that difference in pH level provides a different surface structure. As mentioned earlier, the difference in structure is not due to the pH effect alone, but also to the consequential effect of the pH-adjusting chemical - the zinc carbonate hydroxide.

Addition of glycine and dextrin

Further variation in bath composition by the addition of glycine and dextrin to the acid solution

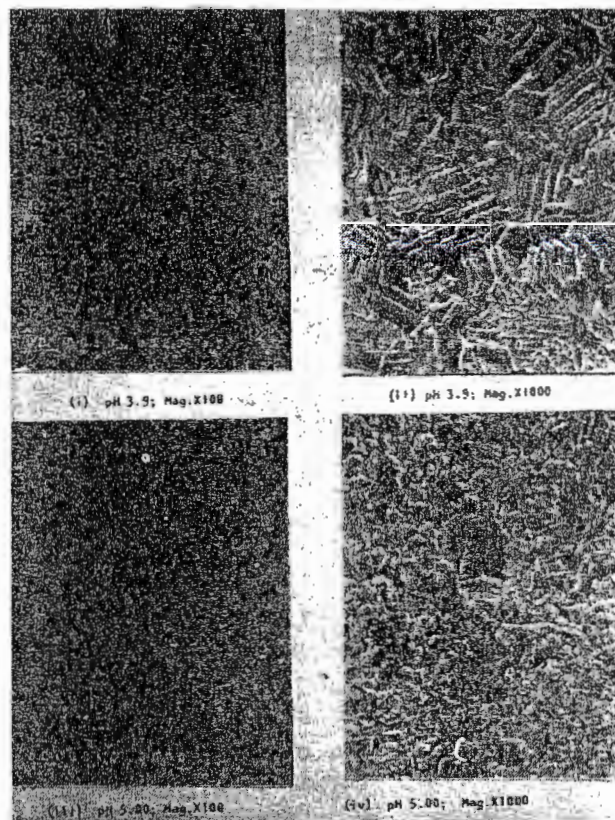


Fig.7. SEM micrographs showing the effect of glycine (2.5g/l) and dextrin (3g/l) on the electrodeposition of zinc on mild steel in acid chloride solution; plating time 12.5min.

at pH3.9 produces a completely different surface structure from all those previously discussed. Fig.7(i-ii). At x100 magnification, (Fig.7(i)), the real crystal structure is not discernible. There is a complete absence of pores, and the compactness of the zinc deposition is very clear. At the higher magnification of x1000, Fig.7(ii), the crystal structure is uniquely clear. The surface crystals are in platelet-like form and arranged all over the surface in piles of different orientations. At this pH level it is apparent that the zinc electrodeposition is good. It is not clear, however, which of the additives has a greater influence on this unique surface structure. Their effect is probably synergistic.

On re-adjusting the pH of 3.9 to 5 with zinc carbonate hydroxide, at the same bath composition and for the same plating duration, a completely different surface crystal structure from the above is obtained. Fig.7(iii-iv). The surface crystals are smaller and are in amorphous/angular shapes all over, without any particularly defined arrangement (Fig.7(iv)). There are no pores observed at both low (Fig.7(ii), x100) and high, (Fig.7(iv), x1000), magnifications, an indication that a good plating is obtained. It could be said that the effect of pH variation is more one of modifying the surface structure, the technical effect of which has not yet been determined.

Addition of glycine and thiourea

Glycine (2.5g/li) and thiourea (0.75g/li) addition to the acid solution at pH3.9 and for a plating time of 12.5min provides a porous result as shown in Fig.8(i-ii). The plating porosity is clear at the low-magnification of $\times 100$ (Fig.8(i)). At the higher magnification of $\times 1000$, (Fig.8(ii)), it is clearer that the electrodeposition is not good. Further repeated experimental work could not provide a better result either. The reason for this poor plating with the use of glycine and thiourea together is not understood. It might be that the experimental work in this particular regard is faulty, or the additives enhance the poor throwing-power of the bath instead of improving it.

Readjustment of the bath pH level from 3.9 to 5 with zinc carbonate hydroxide did not provide a better result, Fig.8(iii-iv); in fact, it produced a worse result. The bath composition here, with the use of glycine and thiourea as additives, could be described either as not suitable for zinc electrodeposition on mild steel in acid solution, or the operating parameters (in particular the pH requirement) is sensitive, and the right pH level suitable for good electrodeposition has yet to be used for this bath with these additives.

Conclusion

1. The addition to acid-solution, in turn, of thiourea and dextrin; thiourea, dextrin and glycine; and glycine and dextrin, gives good zinc electrodeposition on mild steel without any pores being observed at both pH4 and pH5 for a plating time of 12.5mins.
2. The combined additives, representing different bath compositions, give different surface structures at both pH4 and pH5.
3. The plating time of 12.5mins for each of the electrodeposition operations was generally found suitable throughout this investigation.
4. The additives used and the pH levels at which this investigation was carried out, in addition to the plating time mentioned in (3), are generally found suitable for zinc electrodeposition on mild steel in acid solution, with the exception of the addition of combined glycine and thiourea

Acknowledgement

This work was carried out by one of the authors (Dr C.A.Loto) with financial assistance (fellowship) from the Swedish Institute, Stockholm, and travelling sponsorship from the Federal Ministry of Science and Technology, Lagos, Nigeria, to whom the authors are grateful. The co-operative laboratory assistance of Messrs Goran Fritze and

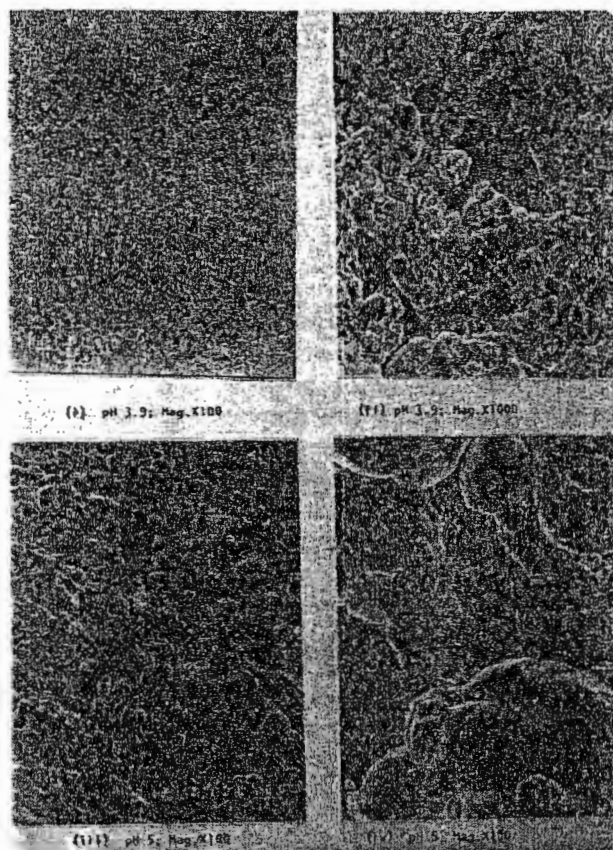


Fig.8. SEM micrographs showing the effect of glycine (3g/li) and thiourea (0.75g/li) on the electrodeposition of zinc on mild steel in acid chloride solution; plating time 12.5min.

Urban Jelvestam from the Department of Engineering Metals, Chalmers University of Technology, Gothenburg, is highly appreciated.

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