# Duplex Zinc + Zinc-Tin Alloy Coating with High Corrosion Resistance

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Duplex zinc-tin coatings were obtained by displacement deposition of tin layer on the electrolytic zinc coating. Further heat-treatment (100-200 °C) produced thin layer of zinc-tin alloy with tin content changing from 10 to 90% at the surface and approaching zero at the depth of 2 to 6 μm. Concentration profile across the coating depends mainly on the temperature and time of heat-treatment. Coatings have shown higher corrosion resistance in 5%-ig NaCI and longer protection of steel base in salt-spray tests.

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## Introduction

A number of electrodeposited zinc-based alloys have shown better protection of steel against atmospheric corrosion and in certain cases may be considered as an acceptable substitute for cadmium. Zn-Sn alloy (60-80 Sn %) is considered as one of such prospective coatings on steel, however actual composition of Zn-Sn electrodeposits may vary considerably over the surface of plated parts due to nonuniform distribution of current density. Apart from that unavoidable changes in the ionic composition of the plating bath will cause additional deviation in the composition of the coating.

By the deposition of layers of individual components, Zn and Sn, followed by heat treatment Zn-Sn alloy with Sn-to-Zn ratio varying across the coating can be obtained. Corrosion of such coating and its protective properties will depend on the total coating thickness, its average composition and on the distribution of the components across the coating.

In the present work Zn-Sn alloy coatings were obtained by the electrodeposition of Zn layer followed by immersion (displacement) formation of tin layer. In the course of the next step – heating in the normal atmosphere – diffusion process of Sn and Zn in the opposite directions takes place (Fig. 1).

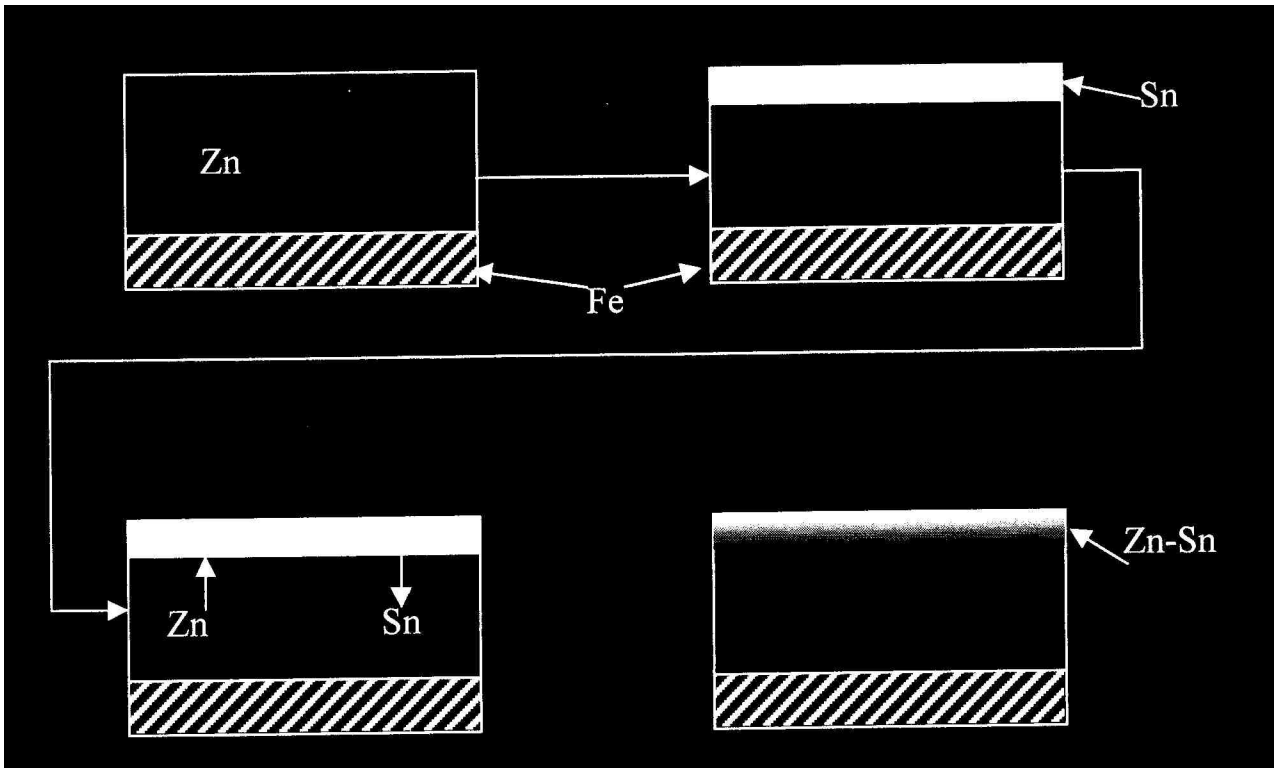



*Fig 1. Formation of Zn-Sn coating.*

## Experimental Procedure

Table 1. Composition of Tin Immersion Coating Solutions

| Components, g/l | Solution #1 | Solution #2 | Solution #3 |
|---|---|---|---|
| $SnSO_4$ | 20-25 | 10-15 | 5-50 |
| $K_4P_2O_7$ | 200 | - | - |
| Malonic acid | - | 70 | - |
| $H_2SO_4$ | - | - | 1.5-2.0 |
| $(NH_4)_2SO_4$ | 5 | - | - |
| Proprietary additive #1 | - | 1-2 | 1-2 |
| Proprietary additive #2 | - | - | 1-2 |
| pH | 7.5-8.0 | 5,5-6,0 | 1.0-1.5 |
| T, °C | 18-25 | | |

Zn layer 10 μm thick was deposited on steel base from the solution $ZnSO_4 \bullet 7H_2O$ 140 g/l; $(NH_4)_2SO_4$ 2 g/l; $NH_4CI$ 10 g/l; $H_3BO_3$ 15 g/l; proprietary brightener, at pH 4.5-5.0, 20 °C and 1 $A/dm^2$. After rinsing and drying the specimens were heated in the normal atmosphere at 100-200 °C. Corrosion tests were made by immersion into 5% NaCI and by salt-spray test.

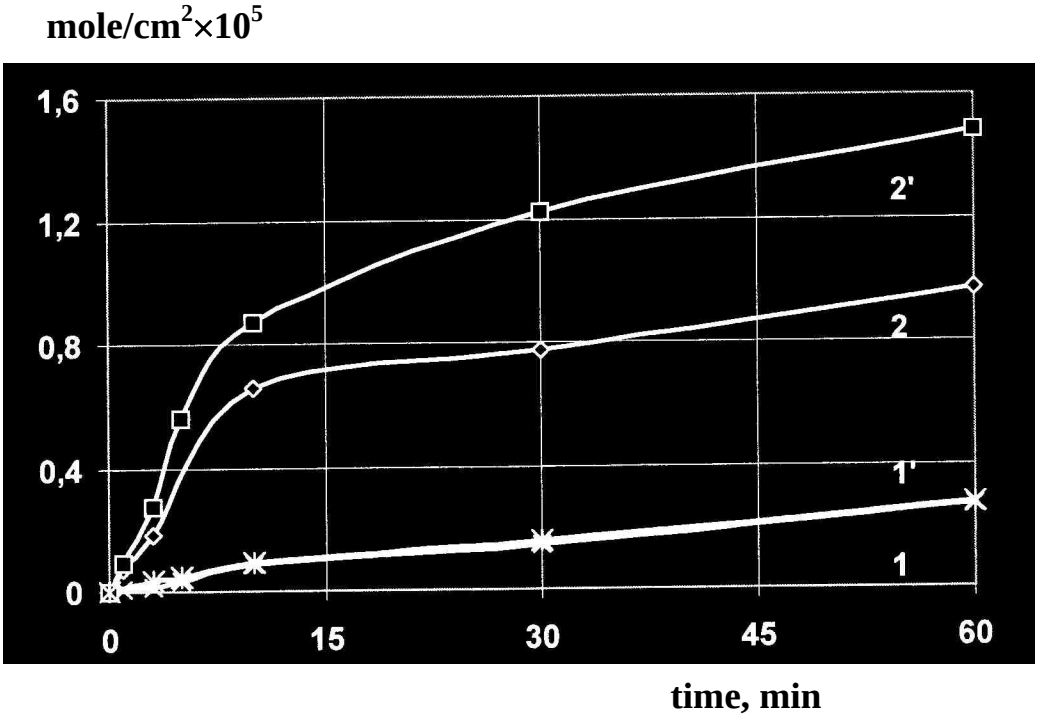



*Fig 2a. Formation of immersion tin layer and dissolution of zinc in solution #1 (1, 1') and in solution #2 (2, 2'). 1, 2, Sn; 1', 2', Zn.*

Comparative tests were made for the specimens with pure Zn coatings (both as plated and subjected to passivation in chromate solution) and for specimens with different types of Zn-Sn coating (includings those subjected to chromate treatment).

## Results and Discussion

Maximum tin layer thickness was reached within few minutes in the solution #3, while the displacement reaction in the solutions #1 and #2 proceeded much slower (Figs. 2a & 2b). It follows from the position of the curves for the deposition of tin and dissolution of Zn that in addition to the displacement reaction hydrogen evolution may also take place (solution #2 and solution #3 at lower tin salt concentration). Conditions of heat treatment (temperature and duration) play decisive role in the formation of the layer with varying tin-to-zinc ratio (Figs. 3a & 3b). Zn-Sn coating containing 60 to 80 % of tin was reported [1] to ensure good protection of steel. Relatively thick (0.5 to 0.7 μm) outer part of the coating with Sn content 60 to 80 % corresponds to the temperatures of 185 to 195 °C and the treatment time 120 to 150 min.

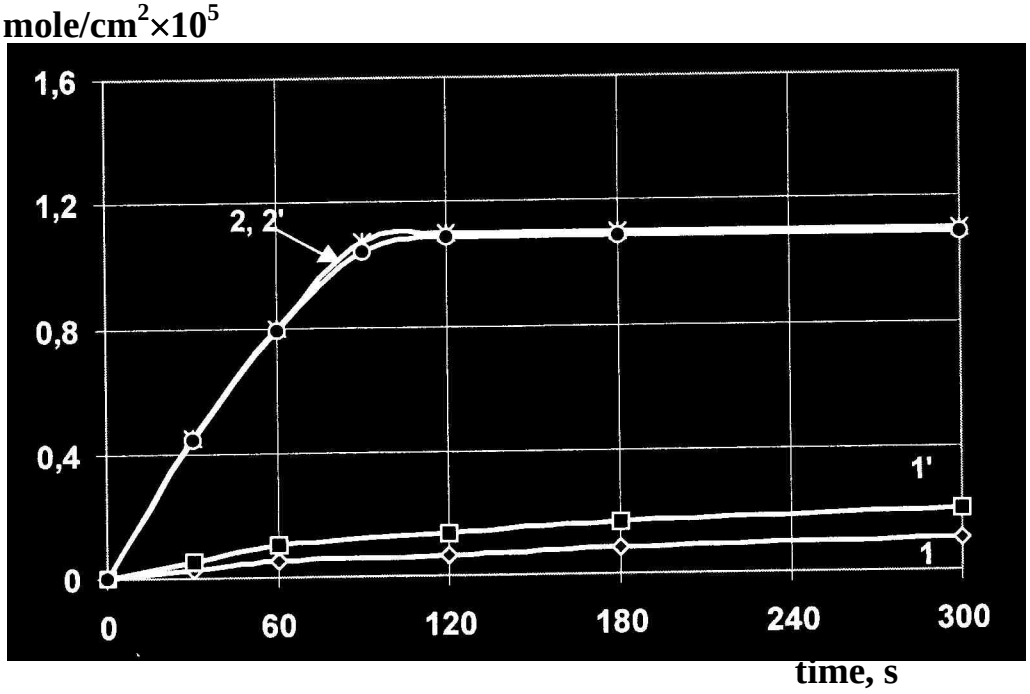



*Fig 2b. Formation of immersion tin layer and dissolution of zinc in solution #3.*
*1, 1', $SnSO_4$ 5 g/l; 2, 2', $SnSO_4$ 50 g/l; 1, 2, Sn; 1', 2', Zn.*

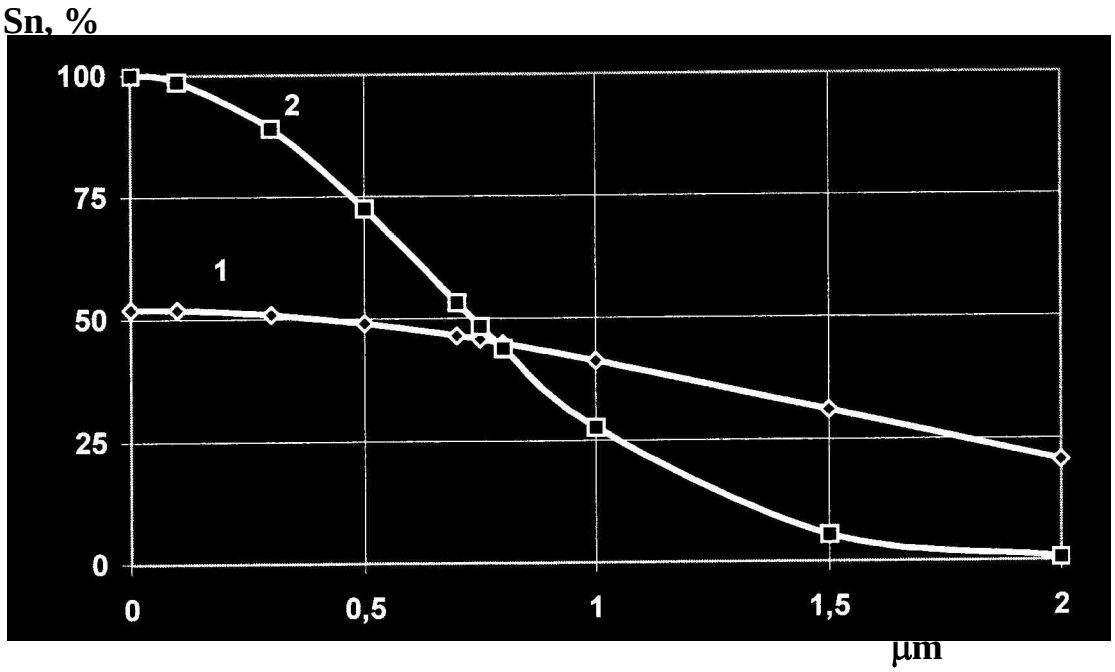



*Fig. 3a. Distribution of Sn in the coating; solution #3, $SnSO_4$ 50 g/l.*
*1, thermal treatment 210 min at 195 ℃; 2, thermal treatment 90 min at 180 ℃.*

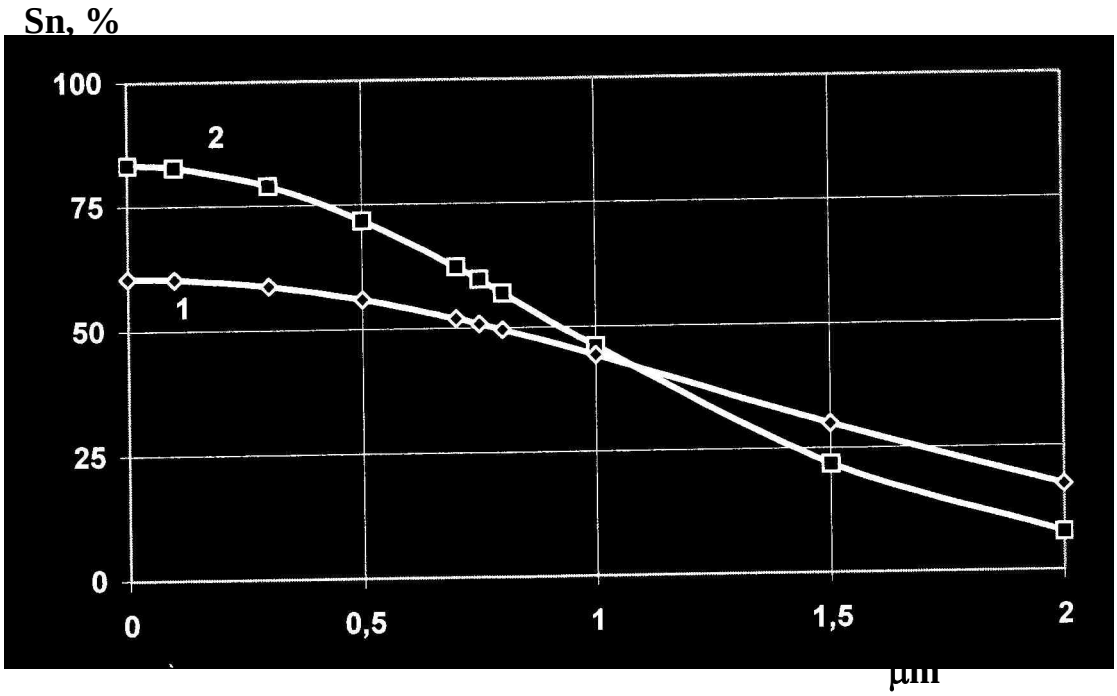



Fig. 3b. Distribution of Sn in the coating; solution #3, $SnSO_4$ 50 g/l.
1, thermal treatment 155 min at 195 °C; 2, thermal treatment 145 min at 185 °C.

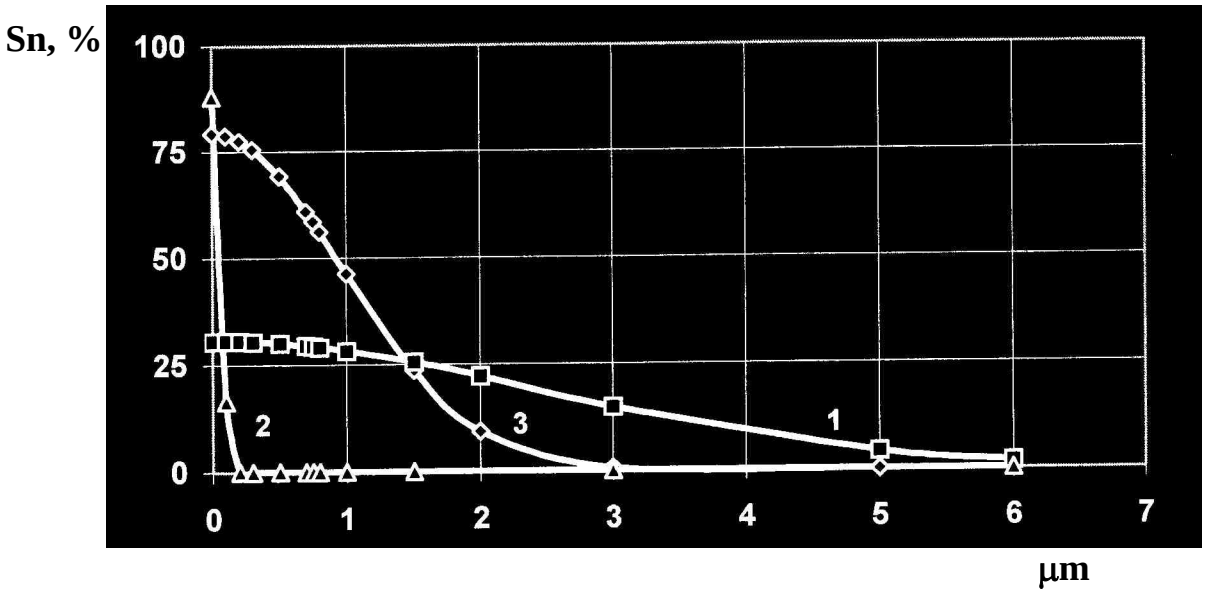



Fig. 4. Distribution of Sn in the coatings subjected to corrosion tests (See Fig. 5). 1, Sn, 2 μm; 800 min; 190 °C; 2, Sn 0.12 μm; 30 min; 125 °C; 3, Sn 2 μm; 120 min; 190 °C.

Corrosion tests were made for specimens represented in Fig. 4. All three types of specimens have shown certain improvement in their corrosion resistance in the tests by immersion into 5 % NaCI (Fig. 5). An obvious improvement was also observed in salt-spray tests (Fig. 6). Additional passivation treatment of the coatings in chromate solution produces much stronger effect on pure Zn coatings rather than an Zn-Sn ones.

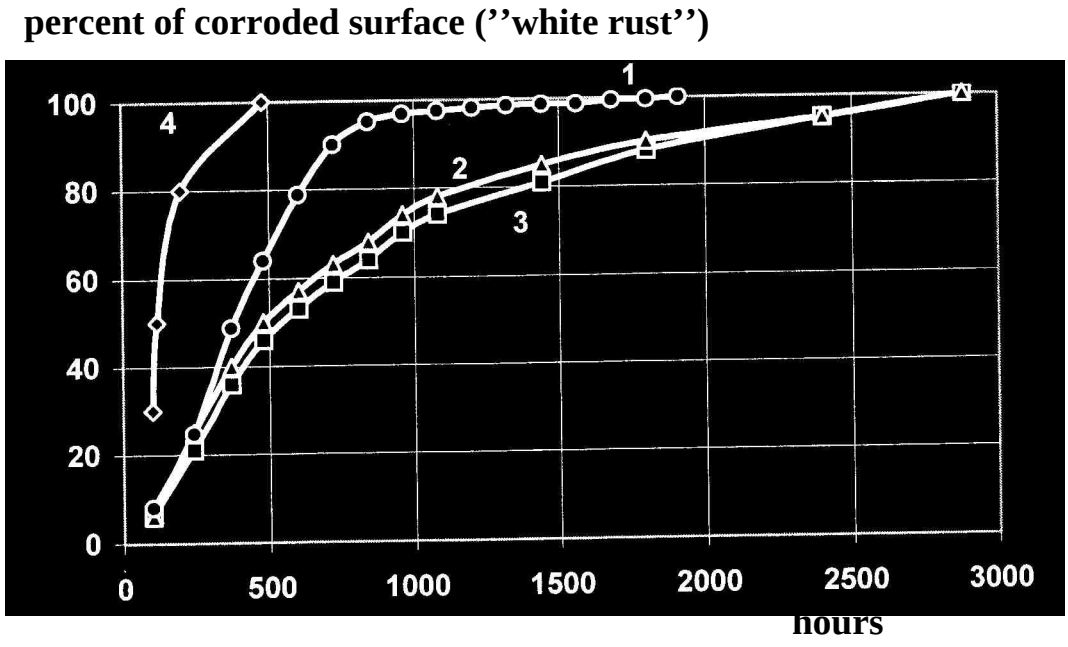
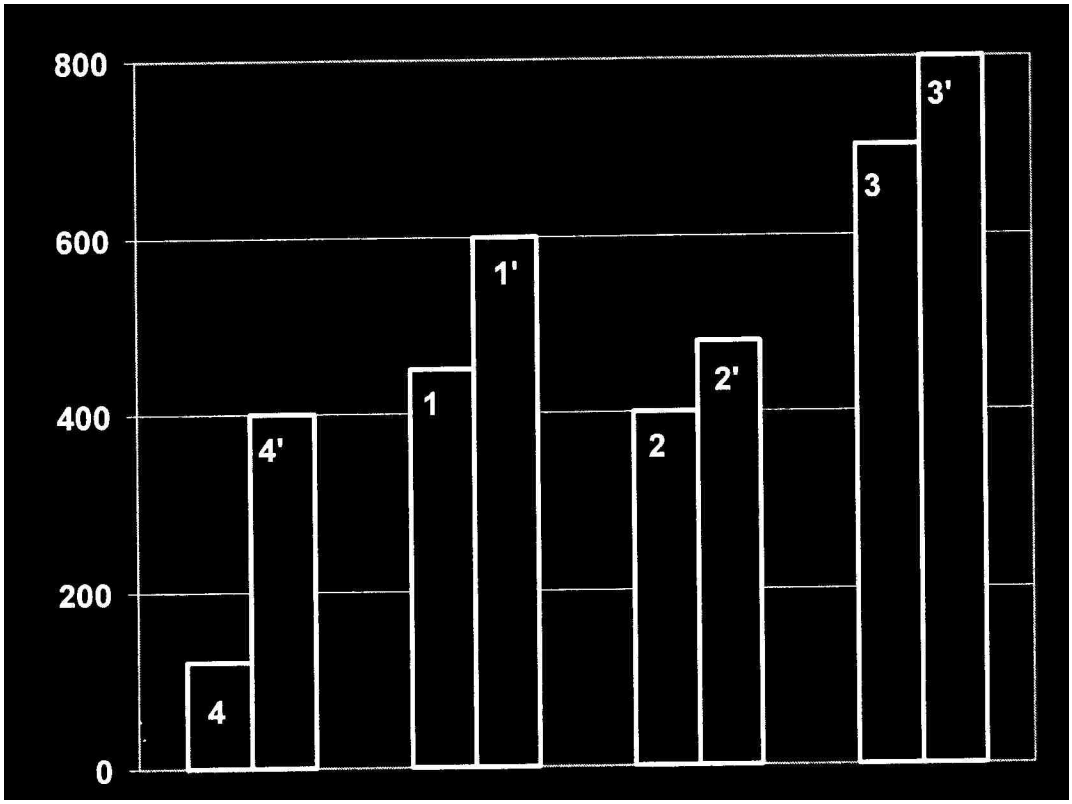



Fig. 5. Corrosion tests of the coatings made by immersion into 5% NaCl solution.
1, 2, 3 – See Fig. 4; 4, pure Zn coating.




Fi. 6. Results of corroson tests in salt-spray chamber. 1-4, nonchromated coatings (See Fig. 4 & 5); 1'-4', same coatings after passivation in chromate solution.

**Summary**

Corrosion resistance of ordinary zinc coatings can be improved by additional post-treatment process: formation of immersion tin layer (~2 μm thick) by displacement reaction followed by heat-treatment to produce thin (~1μm) layer of Zn-Sn alloy.

[1] J. Raub, W. Pfeiffer, M. Vetter. Galvanotechnik, 1979, 70, #1, p.7.