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ELECTRODEPOSITION OBTAINING AND CORROSION BEHAVIOUR OF PHENOL FORMALDEHYDE RESIN/ZINC COMPOSITE COATINGS

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ABSTRACT

The present work has the purpose of obtaining composite coatings in zinc matrix by using phenol - formaldehyde resin type NOVOLAC (RESITAL 6358/1) in the electrodeposition process of zinc. The PF resin/Zn composite coatings were electrodeposited from a suspension of PF resin particles (diameter < 56 μm) in aqueous zinc sulphate electrolyte. Suspension was prepared by adding 10g/L and 25g/L PF resin particles into solution. The pure zinc coating has a rather regular surface, whereas the composite coatings surface has fine surface structure. For layers obtained at 3A/dm^2 the polarization resistance is higher for composite coatings with 10 g/L PF resin (R_p = 238.75 Ω cm^2) than pure zinc (R_p = 34.54 Ω cm^2). For layers obtained at 5A/dm^2 the polarization resistance is higher for composite coatings with 25 g/L PF resin (R_p = 430.19 Ω cm^2) than pure zinc (R_p = 127.34Ω cm^2). As test solution 0.5M sodium chloride was used, it was observed that by adding PF resin particles in zinc electrolyte for electrodeposition it was obtained a very good distribution of resin particles on zinc surface and PF resin/Zn composite coatings obtained are most resistant at corrosive attack than pure zinc obtained from electrodeposition under the same conditions.

KEYWORDS: PF resin particles, electrodeposition, PF resin/Zn composite coatings, thickness layers, polarization resistance

1. Introduction

Metal composite materials have found application in many areas of daily life for quite some time. Often it is not realized that the application makes use of composite materials. These materials are produced in situ from the conventional production and processing of metals. For many researchers the term metal matrix composites is often equated with the term light metal matrix composites (MMCs). Substantial progress in the development of light metal matrix composites has been achieved in recent decades, so that they could be introduced into the most important applications. These innovative materials open up unlimited possibilities for modern material science and development; the characteristics of MMCs can be designed into the material, custom-made, dependent on the application. From this potential, metal matrix composites fulfill all the desired conceptions of the designer [1]. However, the technology of MMCs is in competition with other modern material technologies, for example powder metallurgy. The advantages of the composite materials are only realized when there is a reasonable cost – performance relationship in the component production. The use of a composite material is obligatory if a special property profile can only be achieved by application of these materials [2].

To summarize, an improvement in the weight specific properties can result, offering the possibilities of extending the application area, substitution of common materials and optimization of component properties. With functional materials there is another objective, the precondition of maintaining the appropriate function of the material.

Objectives are for example: increase in strength of conducting materials while maintaining the high conductivity, improvement in low temperature creep resistance (reactionless materials), improvement of burnout behavior (switching contact), improvement of wear behavior (sliding contact), increase in operating time of spot welding electrodes by reduction of burn outs, production of layer composite materials for electronic components, production of ductile composite superconductors, production of magnetic materials with special properties. For other applications, different development objectives are given, which differ from those mentioned before. For example, in medical technology, mechanical properties, like extreme corrosion resistance and low degradation as well as biocompatibility are expected [3]. For all these reasons metal matrix composites are only at the beginning of the evolution curve of modern materials (see Fig. 1) [4].

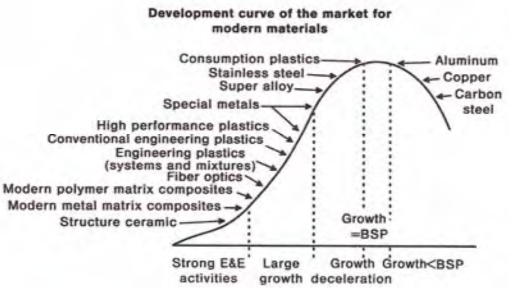

Fig. 1. *Development curve of the market for modern materials*

Zinc is the most widely used material for protection of steel against corrosion. The success of using zinc as a steel coating can be attributed to its sacrificial nature, low cost and ease of application (hot – dipping or electroplating) [5]. Zinc is more corrosion resistant than steel in most natural atmospheres, the exceptions being ventilated indoor atmospheres where the corrosion of both steel and zinc is extremely low and certain highly corrosive industrial atmospheres. The major drawback of thick coatings is poor weldability and difficulty to achieve a specular finish after painting. This provides the need to develop thinner electrodeposited coatings with improved properties such as hardness, ductility, corrosion, etc [6].

Electrodeposition offers rigid control of film thickness, uniformity and deposition rate and is especially attractive owing to its low equipment cost and starting materials. Due to the use of an electric field, electrodeposition is particularly suited for the formation of uniform films on substrates of complicated shape, impregnation of porous substrates and deposition on selected areas of the substrates [7].

The use of zinc-plated articles is increasing due to its sacrificial protection of steel from corrosion.

This sacrificial protection is due to the fact that the zinc is a less noble metal and catholically protects the steeleven in places where the deposit is damaged. Zinc coatings are obtained either from cyanide, non-cyanide, alkaline or acid solutions [8 - 12]. Because of the pollution and high cost associated with cyanide, deposition from other baths such as sulphate, chloride and mixed sulphate-chloride baths are gaining importance.

Good deposition depends mainly on the nature of bath constituents. Generally, a plating bath contains conducting salts, buffering agents, complexing agents and metal ions. Among these the complexing agents effectively influence the deposition process, solution properties and structure of the deposit. The action of these complexing agents is specific and depends on pH, nature of anion, temperature and other ingredients of the medium. Too many ingredients cause difficulties in maintaining the operating parameters of the bath solution during the plating process. Some of these agents smoothen the deposit over a wide current density range and the other addition agents influence the production of bright deposits [13].

In the present work, efforts have been made to develop a bath solution without additive because they could give reactions with PF resin particles and the results could not be interpreted properly.

Phenol and formaldehyde are among the most basic building blocks in polymer chemistry. The condensation reaction may be initiated by a number of alkali or acidic catalysts, resulting in a polymer. This polymer, in conjunction with various organic and inorganic reinforcing systems, offers a variety of unique properties and characteristics. The polymer acts as a matrix for binding together a number of substrates such as wood, paper: fibbers (e.g., fibreglass), or particles (e.g. wood flour, foundry sand) to form a highly crossed-linked composite. The phenolic based products have some characteristics: dimensional stability at elevated temperatures; creep resistant, excellent fire performance, cost effective, outstanding durability, excellent strength-to-weight ratio, excellent thermal insulation properties, excellent sound-damping properties, corrosion resistant, water-resistant.

The present work has the purpose of realization of composite coatings obtained by using PF resin type NOVOLAC with commercial name RESITAL 6358/1 (for the first time) synthesised by HÜTTENES - ALBERTUS Germany electrodeposited with zinc. It is necessary to note that by involving the particles of PF resin in a zinc matrix we can obtain materials with properties differing from those of the individual materials.

2. Experiment

For electrodeposition we used a cell shown in Fig. 2. Zinc plate of 99.9% purity was used as anode.

As cathode we used steel plates DC04 (chemical composition and mechanical properties are presented in Table 1) which were degreased with alkaline solution (Na_2HPO_4 x $12H_2O$ 50 – 60g/L, Na_2SiO_2 x $5H_2O$ 25 – 30g/L, liquid soap 2 – 3g/L, temperature 80 – 90^{0}C, time 10min), after etching with HCl15% for 1 - 2min and washing with distilled water.

***Table 1.** Chemical composition and mechanical properties for steel DC04*

Steel	Chemical composition,%						Yield strength N mm^{-2}	Max tensile strength N mm^{-2}	Min % total elongation 80mm GL
	C	Mn	Si	P	S	Al			
DC04	0.04	0.20	0.02	0.018	0.012	0.060	210	270 – 350	38.00

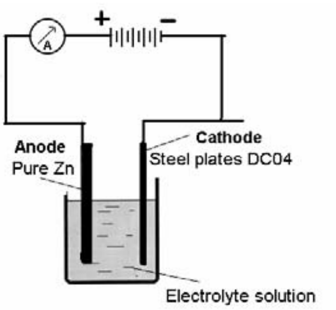

***Fig. 2.** Cell for electrodeposition*

The PF resin/Zn composite coatings were obtained from a suspension of PF resin particles (diameter < 56 μm) in aqueous zinc sulphate electrolyte (Table 2).

***Table 2.** Composition and operating conditions for electrodeposition*

$ZnSO_4$ x $7H_2O$	310g/L
Na_2SO_4 x $10H_2O$	75g/L
$Al_2(SO_4)_3$ x $18H_2O$	30g/L
PF resin particles	10g/L and 25g/L
Temperature	25^{0}C
pH	3.5 – 4.0
Current density	3A/dm^2 and 5A/dm^2
U	1V
Time	1h
Stirred	1000 rpm

Zinc sulphate electrolyte has cathodic polarization bigger than zinc chloride electrolyte so that we used sulphate electrolyte for electrodeposition. Sodium sulphate increase the conductibility and ability to disperse and aluminum sulphate was used as buffering agent which stabilized the acidity of electrolyte. Concomitantly we obtain more shining layers.

Phenol-Formaldehyde resin is a highly crosslinked thermosetting material that is produced by the poly-condensation of phenol and formaldehyde in the presence of either acidic or basic catalyst. An acid catalyst is usually used in preparing NOVOLAC type of resin. A novolac resin is produced if the mole ratio of formaldehyde to phenol (F/P) is greater than one [14]. This procedure produces relatively linear chains with typical molecular weights between 500 and 1000g/mol (see Fig. 3).

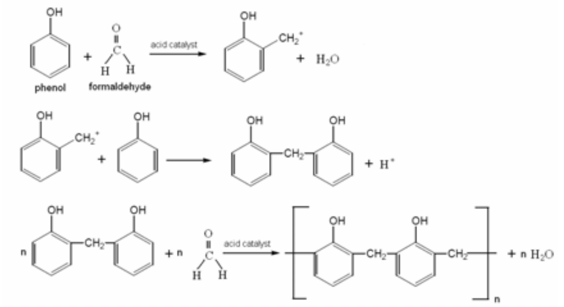

***Fig. 3.** Schematic illustrating the formation of the novolac type structures*

The properties of PF resin type NOVOLAC with commercial name RESITAL 6358/1 synthesised by HÜTTENES – ALBERTUS Germany are presented in Table 3.

***Table 3.** Properties for RESITAL 6358/1*

Melting point	70 – 80 º C
Sliminess at 120^{0}C	35 – 55 Pa·s
Flow length	40 – 50 mm
Phenol	< 1 %
Water	< 0,5 %

For electrochemical corrosion measurements we used a three-electrode open cell with pure zinc and PF resin/Zn composite coatings as working electrode (WE), a platinum gauze as counter electrode (CE) and an Hg/Hg_2SO_4/saturated K_2SO_4 solution electrode as reference electrode (SSE = +670mV/NHE). As test solution 0.5 M sodium chloride was used.

The morphology of deposits was examined by scanning electron microscopy (SEM).

3. Results and discussions

Figures 4 – 7 compare a pure zinc coating and PF resin/Zn composite coating obtained at 3A/dm^2 and 5A/dm^2 current density, 1h stirred at 1000 rpm with different concentration of PF resin particles 10g/L and 25g/L (2000x magnification).

The surface morphology of layers is different compared with pure zinc coated. The pure zinc coating has a rather regular surface, whereas the composite coatings surface has fine surface structure. By increasing the PF resin concentration in the zinc electrolyte the surface structure of composite coating is changed more to finer crystallites. The PF resin acts as reducing the crystals size of electrodeposited zinc during co-deposition. The PF resin could have an inhibition effect of zinc crystals growth and a catalytic effect in increasing nucleation sites.

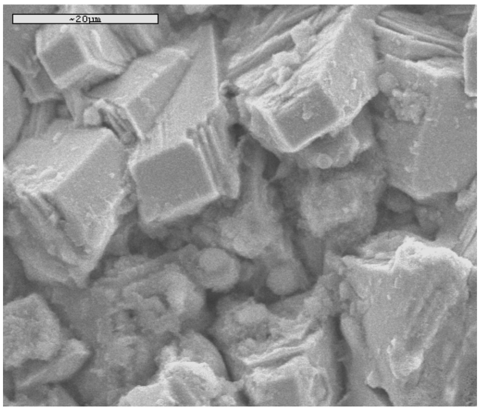

Fig. 4. *SEM surface morphology of pure zinc electroplating obtained at 3A/dm^2 (2000x)*

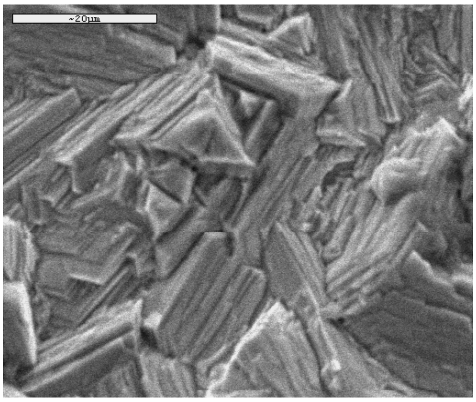

Fig. 5. *SEM surface morphology of pure zinc electroplating obtained at 5A/dm^2 (2000x)*

The thickness of pure zinc layers obtained at 3A/dm^2 and 5A/dm^2 current density, 1h stirred with 1000 rpm is 38.86 µm, respectively 58.24 µm.

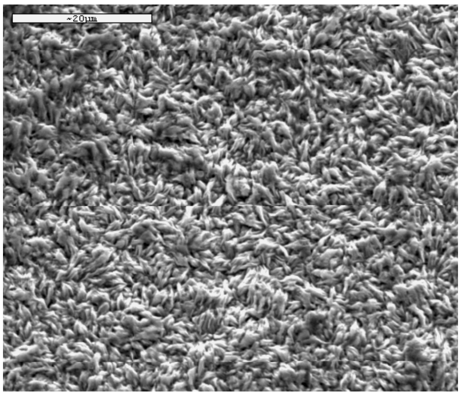

Fig. 6. *SEM surface morphology of PF resin/Zn composite coatings (10g/L PF resin) obtained at 3A/dm^2 (2000x)*

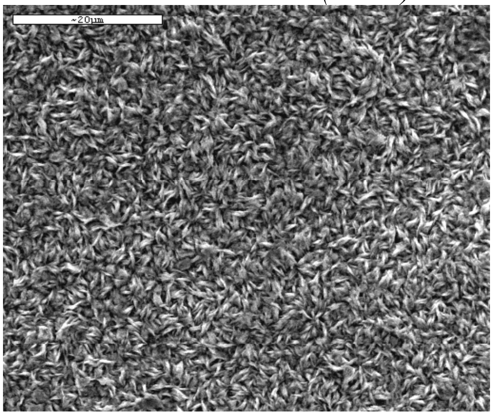

Fig. 7. *SEM surface morphology of PF resin/Zn composite coatings (25g/L PF resin) obtained at 5A/dm^2 (2000x)*

By adding PF resin particles the thickness of layers obtained in same conditions is a little smaller 34.27 µm for layers obtained by electrodeposition process with 10g/L PF resin at 3A/dm^2 and 55.19 µm for layers with 25g/L PF resin at 5A/dm^2 (Figure 8).

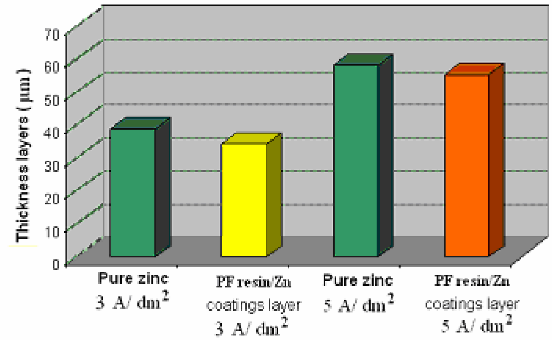

Fig. 8. *Comparative thickness of pure zinc and PF resin /Zn layers obtained by electrodeposition at 3A/dm^2 and 5A/dm^2 with 10g/L, respectively 25g/L PF resin in electrolyte solution*

We could observe that if we increase the current density the thickness of pure zinc and coatings layers increase. By adding PF resin particles in electrolyte solution the thickness of layers obtained is lesser, but not too much than pure zinc obtained under same conditions for electrodeposition. The decreases of layers obtained with resin particles may be explained by fine structure of composite particles.

The electrochemical investigation of each sample began with monitoring of the OCP change immediately after the immersion into the testing solutions till reaching a relatively stable stationary value. The performed potentiodynamic diagrams for pure zinc and PF resin/Zn composite coatings in 0.5M sodium chloride are presented in Figure 9.

In corrosion, quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves, using the Stern-Geary equation, as follows [15]:

$$i_{corr} = \frac{1}{2.303 R_p} \left(\frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c} \right) \qquad (1)$$

- i_{corr} is the corrosion current density in Amps/cm^2;
- R_p is the corrosion resistance in ohms·cm^2;
- β_a is the anodic Tafel slope in Volts/decade or mV/decade of current density;
- β_c is the cathodic Tafel slope in Volts/decade or mV/decade of current density;
- the quantity, $(\beta_a \cdot \beta_c)/(\beta_a + \beta_c)$, is referred to as the Tafel constant.

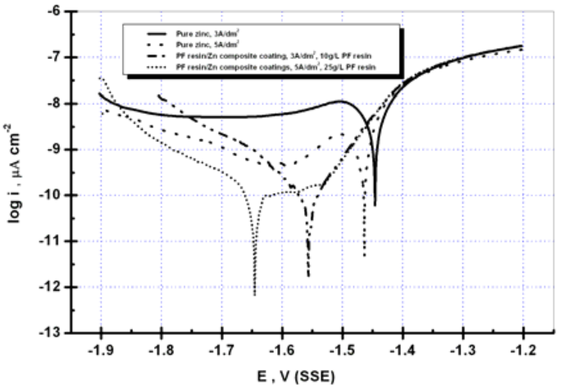

***Fig. 9**. Comparative polarization potentiodynamic curves for pure zinc and PF resin/Zn composite coatings in 0.5M sodium chloride solution obtained after 30 min from immersion time (log scale).*

The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarisation resistance (R_p), which were obtained from the potentiodynamic polarisation curves are summarized in Table 4.

***Table 4.** Polarization resistances values of pure zinc and PF resin/Zn composite coatings calculated from polarization potentiodynamic curves obtained after 30 min from immersion in 0.5M sodium chloride solution*

Type of coatings	**E_{corr}, V;** Hg/Hg_2SO_4	**i_{corr},** μA/cm^2	**β_a,** mV/ decade	**β_c,** mV/ decade	**R_p from Tafel,** Ω cm^2	v_{corr}, μm/year
Pure zinc coating 3A/dm^2	- 1.45	239.98	47.70	31.74	34.54	360.54
Pure zinc coating 5A/dm^2	- 1.47	65.32	40.64	17.50	127.34	89.84
PF resin/Zn composite coating 3A/dm^2, 10g/L resin in electrolyte solution	- 1.53	3.32	32.83	29.30	238.75	34.13
PF resin/Zn composite coating 5A/dm^2, 25g/L resin in electrolyte solution	- 1.64	0.87	26.31	26.93	430.19	5.17

The corrosion potential is shifted to more negative values for PF resin/Zn composite coatings (- 1.64V for coatings obtained at 5A/dm^2 with 25g/L resin in electrolyte solution, respectively - 1.53V for coatings obtained at 3A/dm^2 with 10g/L resin in electrolyte solution) than pure zinc coatings (- 1.47V for coating obtained at 5A/dm^2 and - 1.45V for coating obtained at 3A/dm^2). From potentiodynamic polarization curves the polarization resistance of pure zinc coating obtained at 3A/dm^2 is 34.54Ω cm^2 and for pure zinc coating obtained at 5A/dm^2 is 127.34Ω cm^2 in 0.5M sodium chloride. The polarization resistance of PF resin/Zn coatings are bigger and the values is 238.75Ω cm^2 for coatings obtained at 3A/dm^2 with 10g/L Pf resin in electrolyte solution, respectively 430.19Ω cm^2 for coatings obtained at 5A/dm^2 with 25g/L Pf resin in electrolyte solution in 0.5M sodium chloride solution.

From experimental data was observed that corrosion rate has a big value for pure zinc coatings obtained at 3A/dm^2 (360.54μm/year) and small value for PF resin/Zn composite coatings obtained at 5A/dm^2 with 25g/L PF resin in electrolyte solution (5.17μm/year). It was observed that by adding PF resin particles in zinc electrolyte for electrodeposition it was obtained PF resin/Zn composite coatings most resistant at corrosive attack at 0.5M sodium chloride solution than pure zinc obtained from electrodeposition where the same conditions.

4. Conclusions

Our work proved that PF resin particles type NOVOLAC with commercial name RESITAL 6358/1 could be codeposited with zinc to obtain composite coatings.

The surface morphology of composite coatings layers is different compared with pure zinc coated. The regular crystal structure characteristic of electroplated zinc coatings was disturbed by PF resin particles that perturb the zinc growth during electrodeposition. By adding PF resin in zinc electrolyte for electrodeposition we obtained a very good distribution of PF resin particles on zinc surface.

The corrosion potential is shifted to more negative values for PF resin/Zn composite coatings comparative with corrosion potential for pure zinc coatings.

From potentiodynamic polarization curves the polarization resistance of pure zinc coating obtained at 3A/dm^2 and 5A/dm^2 is smaller than polarization resistance of PF resin/Zn composite coatings obtained under the conditions for electrodeposition. The biggest value of polarisation resistance (430.19Ω cm^2) was obtained for coatings obtained at 5A/dm^2 with 25g/L Pf resin in electrolyte solution in 0.5M sodium chloride

By adding PF resin particles in sulphate zinc electrolyte for electrodeposition we obtain a very fine surface structure of composite coatings, consideredas a method of obtaining nanocomposite coatings and the layers obtained are most resistant at corrosive attack in 0.5M sodium chloride solution than pure zinc obtained from electrodeposition under the same conditions.

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