ELECTRODEPOSITED GALVANIC COATINGS ZnNi - COMPARISON MEMBRANE SYSTEM WITH CONVENTIONAL METHOD

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Abstract

The purpose of these studies is to compare the parameters of the galvanic process using a conventional method for electrodeposition of ZnNi coating with a new method using a membrane system. The study was conducted on a pilot production barrel line using electrolytes operating in industrial conditions. The coating was applied to M6 carbon steel bolts mass-produced and heat-treated. The composition of both baths and their cathode current efficiency was analyzed. The deposition rate and concentration of nickel in the coating were evaluated. Studies have shown a difference in coating deposition rates and in the content of nickel in the coating.

Keywords: Fasteners, alloy coatings, current efficiency, membrane system

1. INTRODUCTION

Nickel plated alloy coatings have been in use since the late 1970s. This trend was initiated by the automotive and aerospace industries at a time when cadmium was considered to be highly toxic [1]. There are three causes why zinc alloys with nickel have been selected.

Firstly the addition of several percent nickel (12-16%) improves of the radically corrosion resistance [2, 3]. The average corrosion requirements for galvanic zinc coatings resistance according to the requirements of the automotive industry are 120 ÷ 240 h (red corrosion), for ZnNi alloys it is 480 ÷ 720 h [4-6].

The second reason for the introduction of nickel into zinc coatings is the use in the cars production light alloy (engine bodies, pumps, brake systems). These elements are connected and fixed by in fastening elements covered with zinc protective coatings. As it is commonly known the connection zinc aluminium is not appropriate due to the difference of potentials of both metals. Adding 14% nickel in the zinc coating reduces its electronegativity and thus minimizes the corrosion effects of the contacts [7]. The standard potential for electrolysis under normal conditions for Zn is - 0.8 V, for Fe - 0.44 V (for Cd - 0.4 V) the potential of ZnNi coating after adding 14% Ni is - 0.55 V [8].

The third reason is the significant increase in hardness of the ZnNi alloy, after adding a few Ni percent the coating HV values 10 times increases. The pure zinc coating has a hardness < 50 HV, alloy coating **ZnNi > 450 HV** [9, 2]. Since zinc is more plastic than steel, static and dynamic stress transfer through threads with zinc coating is limited [10]. The solution is to use a ZnNi alloy coating which hardness is similar like the hardness of the heat treated steel [11]. The high hardness of ZnNi coating increases the wear resistance of the coating, while retaining its ductile properties.

In addition, recent research shows that alloyed zinc coatings with 14-16% Ni protect the base material from hydrogen creating nickel hydride [12].

ZnNi alloy coatings are obtained from two types of electrolyte acid and alkaline baths. However, the automotive industry is recommending alkaline coatings because they are more resistant to corrosion and have better layers distributed on the surface of fasteners [13]. There are currently on the market two different methods for

ZnNi coatings application. The first with a traditional steel anodic system, the other one with the use of selective semipermeable membranes [14]. The purpose of the study was a comparison of the technologies listed above.

2. THE OWN INVESTIGATIONS

2.1. Research facility

Two alkaline electrolyte solutions for ZnNi electrodeposition was chosen for the research - **Figure 1a**. Electrolytes were taken from automated production lines. **Electrolyte 1** comes from the barrel line where the classical electrodeposition method is used, with steel anodes. **Electrolyte 2** comes from the barrel line where the membrane system is used. The investigation regarded screws M 6 - **Figure 1b**, their dimensions with parameters of the electrolysis process shows **Table 1**. The screws were made of carbon steel, cold-formed, hardened and tempered in order to obtain mechanical properties corresponding to the properties of class 8.8. Before coating deposition the classic surface preparation was applied: degreasing, etching, electro degreasing - anodic, activation, neutralization. Additional information: the screw pan head is made of annealing material with higher content of Cr and C.

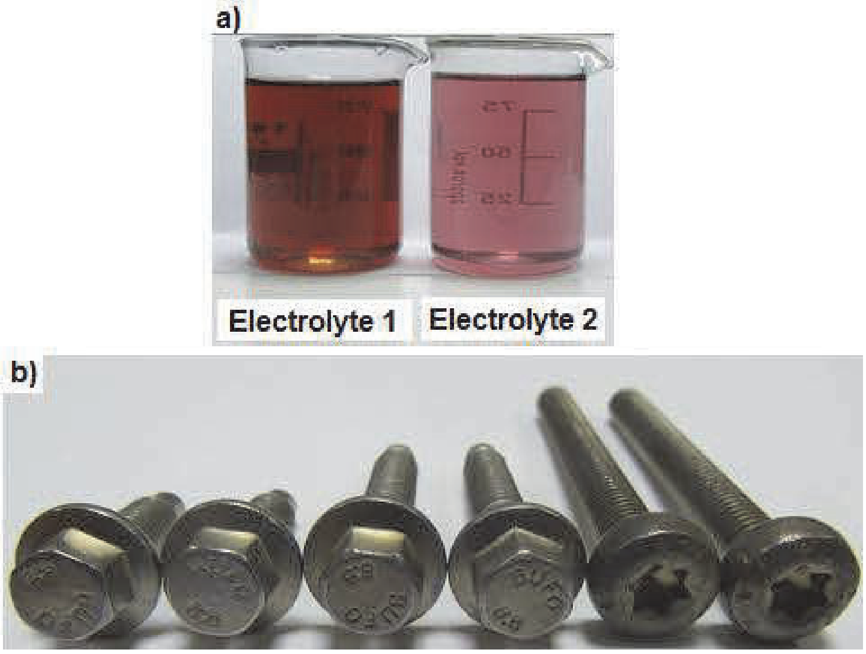


Figure 1 Object of research: a) - an example of the colour of tested electrolytes; b) - tested screw appearance with ZnNi coatings

Table 1 Parameters of electrodeposition process together with screw dimensions

	Flange bolt	Flange bolt	Pan head bolt
Dimension, mm	6x16	6x30	6x55
Weight of 100 pcs.	672.6 g	942 g	1220 g
Area of 100 pcs.	8.953 dm^2	11.975 dm^2	18.159 dm^2
Current density	0.67 A/dm^2	0.67 A/dm^2	0.57 A/dm^2
Temperature of electrodeposition process	22 ^0C	22 ^0C	22 ^0C

3. METHODOLOGY AND THE RESEARCH RESULTS

The study was started from analyzing the composition of the bath by spectrophotometer to determine the working concentrations of basic salts (NaOH, Zn and Ni) and impurities (CO_3^{2-}, SO_4^{2-}) inside the electrolytes working in industrial conditions. Next the cathodic current efficiency based on the theory of Faraday was checked. For this purpose, a nickel anode was installed in a 1 dm^3 vessel and a steel plate was placed in it with width corresponding exactly to the width of the anode. Layout shows **Figure 2**. The plates were weighed before the test. Electrolysis was carried out during 60 min on a sample surface of 0.3 dm^2 with a nominal current of 2.0 A and a current density of 0.15 A/dm^2. The current efficiency of the cathode was calculated from the ratio of mass emitted at the cathode to the mass resulting from Faraday's law.

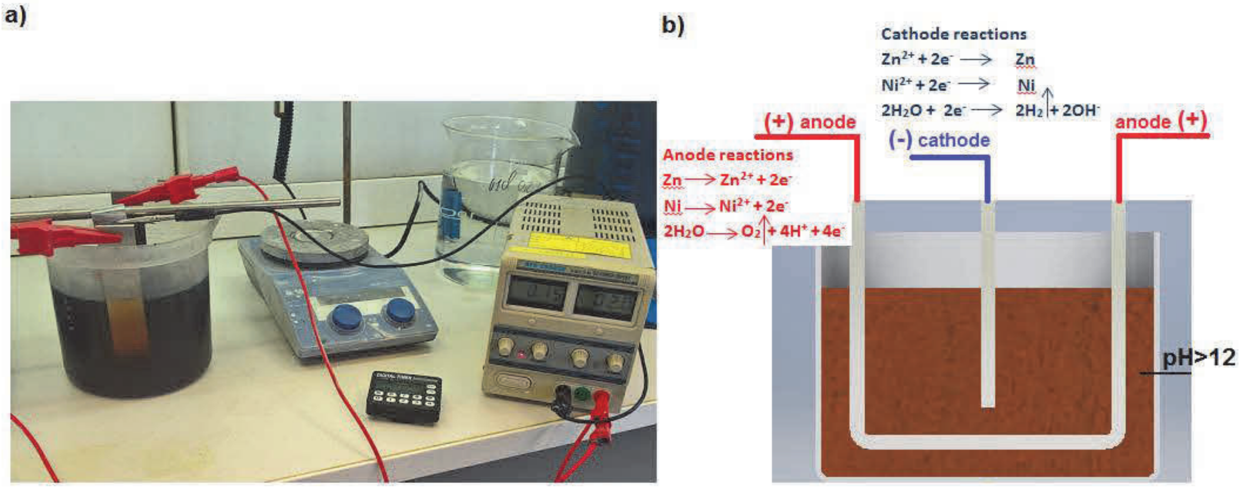


Figure 2 The appearance of: a) - the vessel used to determine current cathode efficiency,
b) - electrolysis scheme along with cathodic and anodic reactions

In the experiment also test to determine concentration of nickel in the coating within the entire current density range was carried out by using a Hull cell. The tile/cathode had dimensions of 20 cm x 7.5 cm. Electrolysis was carried out with a nominal current of 3 A within 20 min. Scheme layout shows **Figure 3**.

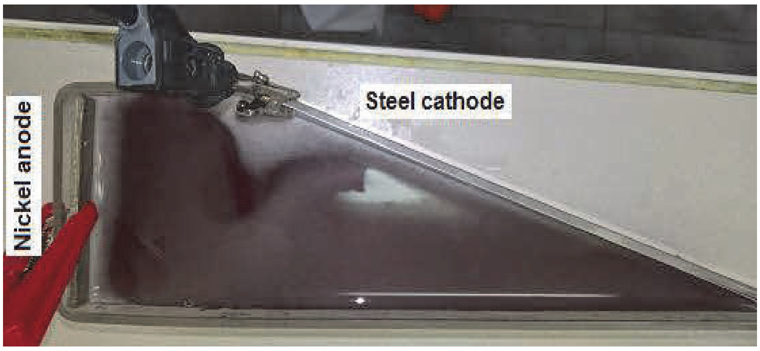


Figure 3 View showing the Hull cell

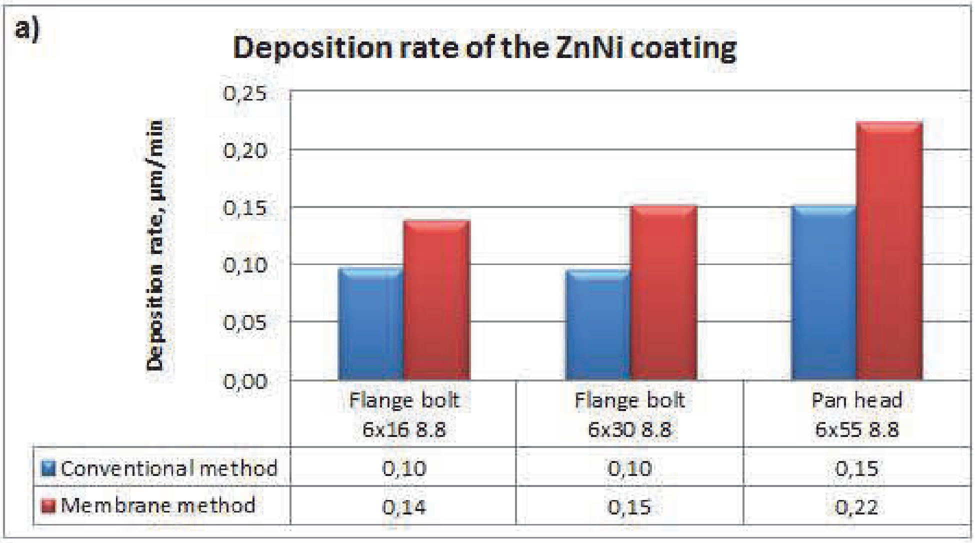
Electrolysis simulations under industrial conditions were carried out on a pilot line located in Research Center of Coventya in France. The screws were placed in a barrel with a load capacity of up to 2 kg, perforation holes of 4 mm. Electrolysis was carried out on all types of screws in both technology, classic and new with ceramic membrane. Thickness and percentage of Ni content in the coating was tested using X-Ray diffraction type Fischer XDVM - W. For each type of screw 6 pcs were randomly selected. Measurement was done on the head of the bolt in half radius distance according to the applicable standards.

Table 2 Parameters of the solutions tested

	Electrolyte 1, conventional method		Electrolyte 2, membrane method		Scope of work recommended by the manufacturer, g/l
	unit	Concentration	unit	Concentration	
Carbonates	g/l	42	g/l	26	Total amount of carbonates and sulphates **< 80**
Sulfur	g/l	43.7	g/l	62.6	
Sodium hydroxide	g/l	105	g/l	122	**120 ÷ 125**
Nickel	g/l	2.57	g/l	1.9	**1.0 ÷ 1.8**
Zinc	g/l	9.06	g/l	7.5	**7.0 ÷ 10.0**
Cathodic current efficiency	**56.5%**		**76.05%**		**n.o.**

Table 3 Result of electrolyte analysis using cell of Hull

	Electrolyte 1, conventional method		Electrolyte 2, membrane method	
Current density	Coating thickness	Concentration of Ni	Coating thickness	Concentration of Ni
11.1 A/dm^2	12.3 µm	13.9%	8.94 µm	14.4%
7.7 A/dm^2	11.5 µm	13.0%	8.04 µm	14.6%
4.1 A/dm^2	8.16 µm	13.1%	6.99 µm	14.4%
1.7 A/dm^2	5.68 µm	13.8%	5.72 µm	14.4%
1.1 A/dm^2	3.45 µm	15.0%	3.68 µm	14.3%
0.7 A/dm^2	2.28 µm	15.0%	2.18 µm	14.2%
0.5 A/dm^2	1.31 µm	14.3%	1.49 µm	13.3%
0.4 A/dm^2	0.69 µm	17.0%	1.02 µm	12.1%
Standard deviation	**4.53 µm**	**1.3%**	**3.09 µm**	**0.857%**



	Flange bolt 6x16 8.8	Flange bolt 6x30 8.8	Pan head 6x55 8.8
🟦 Conventional method	0,10	0,10	0,15
🟥 Membrane method	0,14	0,15	0,22

Figure 4 Graphical representation of results of the evaluation of the rate of electrodeposition: a) - speed of process in µm/min

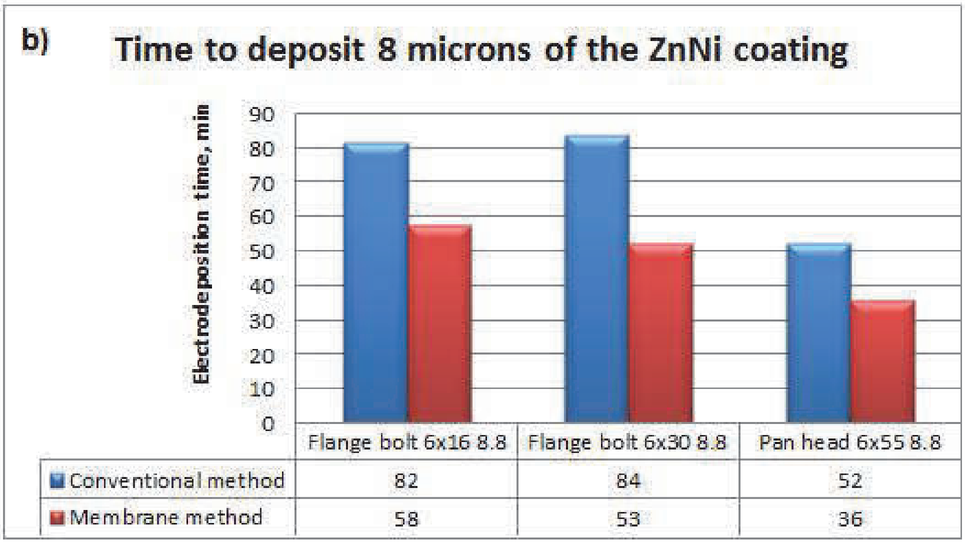


Figure 4 Graphical representation of results of the evaluation of the rate of electrodeposition:
b) - Time required to obtain a coating of min. 8 µm thickness

4. RESULTS DISCUSSION

Comparative studies of two available ZnNi coating electrolysis technologies show the difference between the operational parameters of processes during long-term industrial use.

Electrolyte 1 coming from the classical technology is characterized by lower current efficiency than Electrolyte 2 taken from the line equipped with membrane anodes. The difference between the current efficiency is 20% (**Table 1**).

Both solutions have a high concentration of pollutants, above the values recommended by the chemical manufacturer. The sulphate ions present in the solutions are introduced by $NiSO_4$ salt, which delivers nickel to the electrolyte, thus increases their concentration during the electrolysis - **Table 1**. Carbonate ions are the result of the absorption of CO_2 from the air and the oxidation of the organic compounds used in the electroplating.

Strong extraction of oxygen in the cathode process causes accelerated decomposition. In addition, oxygen supplied from cathode processes takes part in amine decomposition and cyanide nickel complex formation, this negatively affects the cathodic current performance of ZnNi coatings. Brown colour of electrolytes indicates presence of cyanide complexes. The electrolyte 1 is definitely darker than the electrolyte 2 - **Figure 1**. The nickel that is built into the cyanide complex does not participate in the electrodeposition of coating. This results in the higher concentration of this metal in electrolyte 1 (electrolyte 1 - 2.56 g/l, electrolyte 2 - 1.9 g/l) at the same time, lower speed of deposition rate of coating in electrolyte 1 (**Table 2**). In order to separate the anode processes from the electrolyte solution the membrane anodes are used. Membranes bring electrical charge to the electrodeposition but do not allow oxygen to penetrate. Electrolyte 2 is heavily contaminated mainly with sulphates (62.6 g/l - **Table 2**), it suggest that the freezing process is applied on the production line periodically. Despite the high concentration of impurities, the deposition rate of the coating is higher than the viscosity of electrolyte 2 by more than 30% (**Figure 4**). This fact is important for the calculation of production costs and the line production capacity. Low current promotes high quality coatings, lowers energy consumption and chemicals that are dosed according to the amperometric meter indication (Ah). Also the ability to use periodic process freezing generates measurable gains in terms of energy consumption and sludge disposal costs. It follows from the electrolyte test using a Hull cell that for the electrolyte 2, the Ni percentage in the coating over the whole bandwidth of the current density is more uniform than in the electrolyte 1 (**Table 3**).

The above results show yet another regularity. The ZnNi coating electrode deposition rate on the 6x55 screws in both technologies was higher than in the case of others screws, this is related to the type of material used to produce them (**Figure 4**). The wire rod for the 6x55 screws production contains alloyed elements, it was composed of more chromium and carbon (Cr 0.40%, C 0.35 ÷ 0.39%) in comparison to the material used to produce the 6x16 and 6x30 screws (Cr 0.15%, C 0.15 ÷ 0.20%).

5. CONCLUSIONS

Based on the research, the following conclusions can be formulated:

- The use of a membrane system in the galvanic process reduce the process time by about 30%, increasing the deposition rate of the coating,
- Shorter electrodeposition time in membrane technology does not require from manufacturers to lower productivity on line, which contributes to maintaining high productivity and fixed unit production costs,
- Maintaining 75% of cathode currents at high pollutant concentrations results in greater repeatability and quality of coatings without requiring higher current densities,
- Studies have shown that the selective action of membranes effectively lowers the growth of carbonates in the electrolyte. In addition, it significantly reduces the formation of cyanide complexes,
- Reducing the concentration of cyanide complexes makes waste water treatment cheaper, as it does not require breakdown of complexes before precipitating metals,
- Production of alloy coatings using a membrane system offers greater possibilities for process optimization. No limitation from the point of view of production parameters allows optimization of quality and cost parameters.

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