

## CONTINUOUS AND IN-SITU CONTROL OF THE GALVANIC PROCESS BY SPECTROMETERS FLOW-CELLS

GUTT, S[onia]; GUTT, G[heorghe] & POROCH - SERITAN, M[aria]

**Abstract:** The paper presents a galvanic flow-cell for the qualitative and quantitative chemical analysis by spectrophotometric method of the electroplating bath of nickel in the Watts type bath, in order to establish optimal working conditions. The cell allows the qualitative and quantitative evaluation of the electrolyte by the spectrophotometry method. Also, it allows to achieve the materials balance, the energy balance and to calculate productivity by gravimetry.

**Key words:** galvanic, flow-cell, efficiency, productivity.

### 1. INTRODUCTION

In order to determine qualitative and quantitative chemical composition of liquids by the spectral way, in situ and on-line, both in by-pass mode as well as under flow injection analysis (FIA), the special flow cells are used. The column of flow liquid in the special cell is a photometer through a light beam transmitted via an optical fiber assembly from light source to a spectrometer, which is equipped with linear photodiode array as detector (Mallory, 2006). The chemical analysis is performed by automatic interpretation of the spectrograms that the specific absorption wavelength values identify the chemical species present in solution and the peak height is converted into concentration values (Kaim, 2008), Gutt, 2007). Such cells can be used in electrodeposition to determine continuously the concentration of galvanic electrolyte (Gutt, 2010); with the aim of automatic adjustment for the components in galvanic bath concentration without the possibility to determine the current and energy efficiency, without the possibility to determine the material and energy balance and without possibility to determine the process productivity according to specific working parameters (Gutt, 2010).

### 2. EXPERIMENTAL

In the Instrumental Analysis Laboratory of the Faculty of Food Engineering Suceava, a flow cell was developed, built and tested figure 1, figure 2 and figure 3 which allows the qualitative and quantitative evaluation of the electrolyte by spectrophotometry, and achieving the materials and energy balance and the productivity calculation.

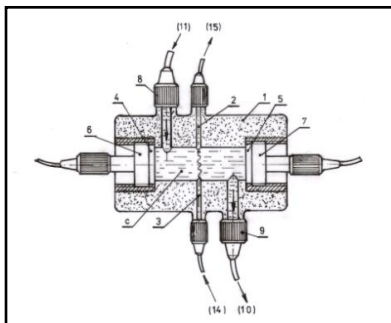


Fig. 1. The section through the flow cell: 1-body cell, c-cylindrical flow channel, 2, 3 - fiber optics, 4 - anode, 5 - cathode 6, 7 - screws, 8, 9 - inlet / outlet socket for the electrolyte

The experimental mode with electrochemical cell is as follows:

1. The galvanic deposition using a reserve of the electrolyte having the same composition as the industrial electrolyte and using same electrical working parameters (voltage and current density) – determines in time the evolution of the composition and concentration electrolyte for galvanic bath and at the same time by conducting the qualitative non-destructive measurements (brightness, thickness, uniformity of metal distribution, microscopic structure, roughness, etc.). The material and energy balance, current efficiency and productivity of industrial galvanic process are calculated with the values obtained and between parameters of work using and the quality galvanic deposit set correlations.

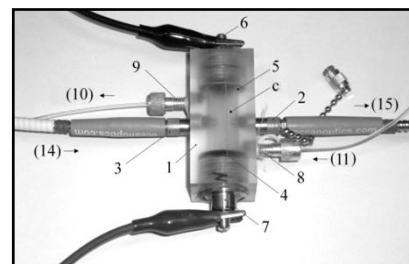


Fig. 2. Imaging of experiments flow cell [Instrumental Analysis Laboratory, Suceava]: 1 - cell-body, 2, 3 - fiber optics, 4 - anode, 5 - cathode, 6, 7 - screws, 8, 9 - inlet / outlet socket for the electrolyte

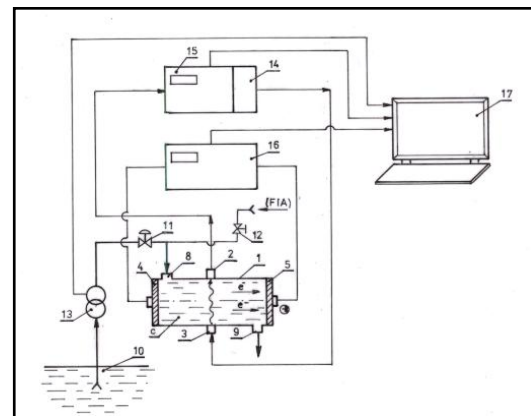


Fig. 3. Schematic diagram of the flow cell: 1 - body cell, c - cylindrical flow channel, 2, 3 - optical fibers, 4 - anode, 5 - cathode, 8, 9 - inlet / outlet socket for the electrolyte, 10 - industrial electroplating bath, 11 - valve for adjusting the flow rate, 12 - valve for flow injection (c.g. FIA), 13 - peristaltic pump, 14 - radiation source, 15 - spectrometer equipped with linear photodiode array as detector, 16 - power supply, 17 - PC

2. The galvanic deposition in parallel with industrial cell using the same electrical parameters of working (voltage and current density), and the addition of other substances into the cell by flow injection analysis (FIA) method, the effect of nature and concentration additives on galvanic deposit quality

are studied. For this purpose the cell electrolyte circuit is interrupted at regular intervals after that the cathode is removed and studied by specific measurements. These measurements reveal the influence of nature and concentration additives (brightening agents, wetting agents, leveling agents, buffering substances, et. al.).

3. The galvanic cell in parallel with the industrial cell using the same electrical parameters of working (voltage and current density), but using different flow rates of galvanic electrolyte, the values showing the influence of convection forced intensity on quantitative and qualitative parameters of deposition are obtained.

4. The galvanic cell in parallel with the industrial cell using the other electrical parameters of working (voltage and current density) - the amount of electrolyte taken through by-pass circuit is extremely small compared to the amount of electrolyte in the industrial bath which allows the work with other process parameters in cell than those in industrial cell. The conclusions obtained are used to optimize the industrial process.

### 3. RESULTS AND DISCUSSION

The use of the flow cell described above made automatically the registration of molecular absorption spectra for the flow electrolyte on three nickel deposits: I - freshly prepared electrolyte, II, III - electrolyte reused, in the sense that it was used in a second, third deposition respectively, the first electrolyte after deposition ceased, Figure 4.

For the three types of electrolytes, the developments of optical absorbance versus time using I experimental mode were followed. The determination results are illustrated in Figure 5, and in the same figure the regression equations are represented and the correlation coefficient describing the experimental changes as well.

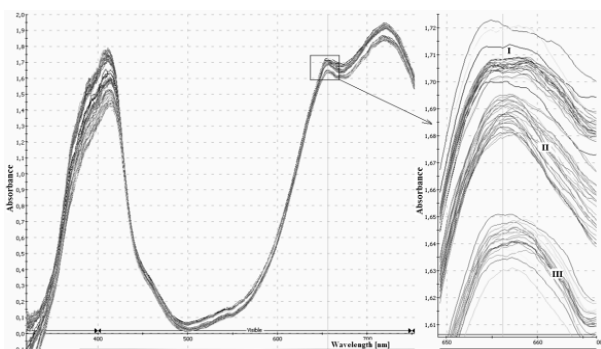


Fig.4. Absorbance variation at a wavelength of 656,17 nm during electrodeposition process with galvanic flow cell for the electrolyte re-circulated in the following technological parameters:  $i = 2,00 \text{ A/dm}^2$ ,  $T = 20,0 \text{ }^\circ\text{C}$ ,  $\text{pH} = 3,5$ ; the recirculation flow of  $0,014 \text{ ml/s}$ ,  $t = 10 \text{ min.}$ , the electrolyte column of photometric =  $7 \text{ mm}$ , I - freshly prepared electrolyte, II, III - electrolyte reused

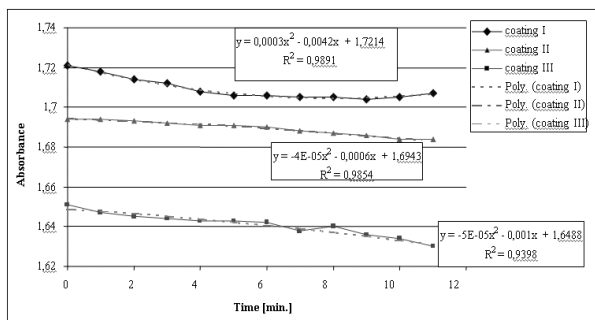


Fig. 5. The absorbance variation of the nickel electrolyte at wavelength of  $656,17 \text{ nm}$  during electrodeposition with re-circulating electrolyte:  $i = 2,00 \text{ A/dm}^2$ ,  $T = 20,0 \text{ }^\circ\text{C}$ ,  $\text{pH} = 3,5$ ; flow recirculation =  $0,014 \text{ ml/s}$ , electrolysis cell volume =  $5 \text{ ml}$ ,  $t = 10 \text{ min.}$ , I - fresh electrolyte, II, III - electrolyte reused, optical path length for electrolyte column of photometric =  $7 \text{ mm}$

For the freshly prepared electrolyte used in the electroplating nickel deposit by the development of absorbance represented in figure 4, a microscopic structure on electron microscope (SEM) at magnification order  $M = 15.000\text{X}$ , figure 7, was performed.

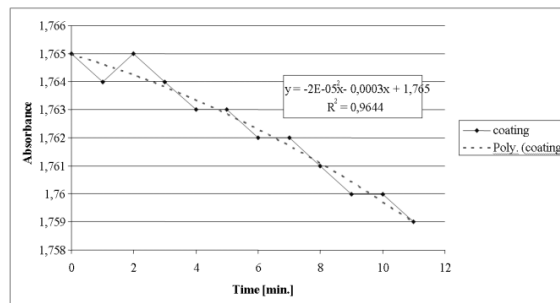


Fig. 6. The absorbance variation at wavelength of  $656,17 \text{ nm}$  of nickel electrolyte in during the electrodeposition process with galvanic flow cell for the stationary electrolyte:  $i = 2,00 \text{ A/dm}^2$ ,  $T = 20,0 \text{ }^\circ\text{C}$ ,  $\text{pH} = 3,5$ ; electrolysis cell volume =  $5 \text{ ml}$ ,  $t = 10 \text{ min.}$ , optical path length for electrolyte column of photometric =  $7 \text{ mm}$ . The electrolyte used was freshly prepared

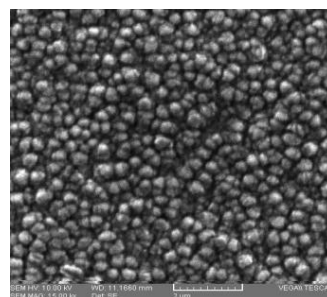


Fig. 7. The microscopic image of the nickel electrodeposit [SEM, VEGA II Tescan,  $i = 2,00 \text{ A/dm}^2$ ,  $T = 20,0 \text{ }^\circ\text{C}$ ,  $\text{pH} = 3,5$ ; flow recirculation =  $0,014 \text{ ml/s}$ ,  $t = 10 \text{ min.}$ ]

### 4. CONCLUSIONS

By the galvanic flow cell above described, an important tool of the qualitative and quantitative investigation for the processes of galvanic metal deposition has been achieved; the cell working to by-pass with an industrial galvanizing bath, without affecting its good functioning. By disconnecting the power source at the two electrodes of galvanic cell it turns into a spectrophotometric flow cell in by-pass mode that allows continuous, on-line and in-situ measurement of galvanic electrolyte composition and concentration in industrial bath. The flow electrolyte changing trough cell allows the study of forced convection effect of electrolyte flow on the quality and quantity galvanic deposit. The cell has a simple construction, easy to clean, it has low cost price and it can be used outside galvanic processes and to study other electrochemical processes such as: electrochemical corrosion, electrorefining, dimensional controlled anodic processing.

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