Pyrophosphate Baths For Palladium-Nickel Alloy Coating: Part II

By Zbigniew Ratajewicz, Czeslaw Saneluta and Józef Sawa

The results of the preliminary investigations of Part I made it possible to carry out laboratory-scale experiments determining the range and direction of the influence of the selected parameters on Pd content of the coatings, as well as cathodic current efficiency and microhardness. The most suitable bath composition and process conditions were selected and the equations connecting chosen properties with bath components and process parameters were obtained.

Experimental Procedure

The experiment was performed according to the plan presented in Table 1, that is, one-sixteenth of the full factorial experiment of type 2^7.* The coating process was performed in a vessel of 150 cm^3 volume, using a Pt sheet as an insoluble anode. The anode-to-cathode area ratio was 2:1. The temperature was thermostatically controlled and the mixing speed limit was maintained by means of a device that put the cathode into to-and-fro motion of 1.2 to 4.8 cm/sec. The coatings intended for composition analysis were obtained on platinic electrodes of 2.0 cm^2 area, protected on one side by a non-conductive coat.

After completion, the alloy coating was dissolved in concentrated HCl, with an addition of one or two drops of H_2O_2. Then, by polarographic method, Pd and Ni contents were determined. The coatings intended for microhardness testing were applied on epoxide-glass laminate samples, covered on one side by a copper foil of 2.5 cm^2 area. Microhardness was measured by the Vickers method and a metallographic microscope, with a load of 2 N. The theoretical thickness of the coatings was established at 5 μm. The experimental conditions, the plan, and the values of the measured quantities are listed in Tables 1 and 2.

With the necessary factors computed and their significance statistically corrected, the following equations were obtained for (Y_1) Pd content in the coatings; (Y_2) cathodic process current efficiency; and (Y_3) microhardness of the coatings:

$$Y_1 = 83.77 + 7.22x_1 - 0.92x_2 + 3.80x_3 + 1.57x_4 - 6.00x_5 - 1.55x_6 + 2.00x_7$$
$$Y_2 = 81.3 + 8.8x_1 + 5.4x_2 + 1.4x_3 + 4.4x_4 - 8.1x_5 + 7.1x_6 + 3.7x_7$$
$$Y_3 = 331.2 - 47.8x_1 + 5.3x_2 - 18.3x_3 + 46.9x_5 + 10.2x_6 - 23.7x_7$$

These equations show that Pd content in the coating depends mainly on: (x_1) Pd concentration in the bath, (x_5) current density, and (x_3) pyrophosphate concentration. Process current efficiency depends primarily on (x_1) Pd concentration in the bath, (x_5) current density and (x_6) temperature, but it is necessary to emphasize that the influence of (x_2) Ni concentration in the bath and (x_4) pH on this characteristic is substantial. Similarly, for the equation for Pd content of the coatings, Pd concentration in the bath, cathodic current density and pyrophosphate concentration exert the most influence on microhardness of the coatings. The directions of the influence of these parameters on microhardness are, however, opposite to the ones on Pd content of the coatings. Either an increase of Pd concentration in the bath or of pyrophosphate concentration decreases microhardness of the coatings, but increase of current density increases it. The substantial influence of mixing speed on microhardness (x_7) in equation (y_3) and the lack of (x_4) pH influence on this quality is worth noting. On the basis of the equations obtained and their graphic presentation in Figs. 1-3, the following composition of the bath and process performance conditions have been chosen to provide alloy coatings with 10 to 20 percent Ni content:

* S.L. Akhnazarova and V.V. Kafarov, Optimizacija eksperimenta v khimii i khimiceskoj technologii, 170, Moskva Vyssaja Skola (1978).

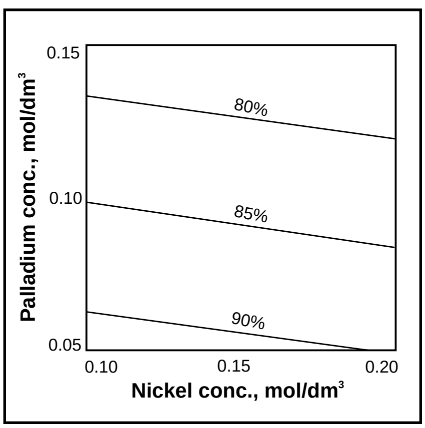


Fig. 1—Effect of Pd and Ni concentrations on Pd content in the coatings with 0.7 mol/dm³ $K_4P_2O_7 \cdot 3H_2O$; pH 8.0; current density, 2.5 A/dm³; 50 °C; cathode motion, 3 cm/sec.

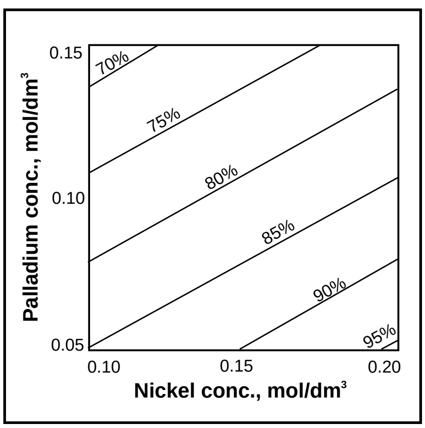


Fig. 2—Effect of Pd and Ni concentrations on process current efficiency with 0.7 mol/dm³ $K_4P_2O_7 \cdot 3H_2O$; pH 8.0; current density, 2.5 A/dm³; 50 °C; cathode motion, 1.2 cm/sec.

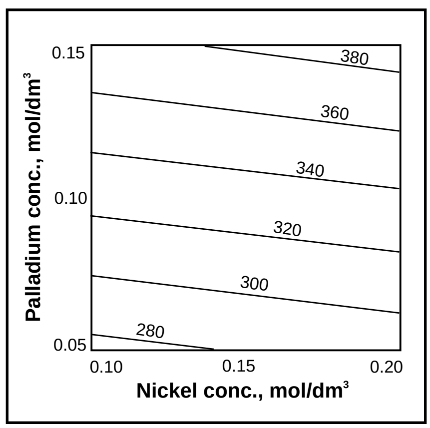


Fig. 3—Effect of Pd and Ni concentrations on Pd content in the coatings with 0.7 mol/dm³ $K_4P_2O_7 \cdot 3H_2O$; pH 8.0; current density, 2.5 A/dm³; 50 °C; cathode motion, 1.2 cm/sec.

Table 1
Experiment Plan and Measured Values

L.p.	x_0	x_1	x_2	x_3	x_4	x_5	x_6	x_7	Y_1	Y_2	Y_3
1	+	–	–	–	+	+	+	+	65.7	65.3	472.9
2	+	+	+	–	+	–	–	–	93.4	95.8	273.6
3	+	–	+	–	–	+	–	+	67.8	60.6	415.7
4	+	+	–	–	–	–	+	+	93.0	97.8	235.9
5	+	–	–	+	+	–	–	+	92.4	77.6	274.5
6	+	+	+	+	+	+	+	+	89.9	104.0	303.7
7	+	–	+	+	–	–	+	–	80.3	86.4	353.1
8	+	+	–	+	–	+	–	–	87.7	62.7	320.2

y_1–percentage Pd content in coating
y_2–cathodic current efficiency
y_3–coating microhardness
(+) upper level, (–) lower level

Table 2
Experimental Conditions

	x_1	x_2	x_3	x_4	x_5	x_6	x_7
Basic level	0.10	0.15	0.70	8.0	2.5	323	3.0
Working step	0.05	0.05	0.10	0.5	1.5	20	1.8
Upper level (+)	0.15	0.20	0.80	8.5	4.0	343	4.8
Lower level (-)	0.05	0.10	0.60	7.5	1.0	303	1.2

x_1–Pd conc. in bath, mol/dm^3
x_2–Ni conc. in bath, mol/dm^3
x_3–$K_4P_2O_7 \cdot 3H_2O$ conc., mol/dm^3
x_4–pH
x_5–current density, A/dm^2
x_6–Temperature, °K
x_7–mixing speed, cm/sec

Table 3
Comparison of Computed
And Measured Pd Contents in the Coatings

Bath composition and parameters		α_k A/dm^2	Pd contents, % computed	Pd contents, % measured
Bath 1		1.0	90.6	90.2
Pd	0.10 mol/dm^3			
Ni	0.20 mol/dm^3	2.0	86.6	86.0
$K_4P_2O_7 \cdot 3H_2O$	0.80 mol/dm^3			
pH	8.0	2.5	84.6	83.0
T	323 K			
v	1.2 cm/s	3.0	82.6	79.5
Bath 2				
Pd	0.125 mol/dm^3	1.0	94.0	95.6
Ni	0.125 mol/dm^3			
$K_4P_2O_7 \cdot 3H_2O$	0.80 mol/cm^3			
pH	8.0			
T	323 K	2.0	92.4	91.1
v	1.2 cm/s			

Pd	0.1 mol/dm^3
Ni	0.2 mol/dm^3
$K_4P_2O_7 \cdot 3H_2O$	0.8 mol/dm^3
pH	8.0
α_k	2.0 to 3.0 A/dm^2
T	50 to 60 °C
v	1.2 cm/sec

To verify the obtained equations (independent of statistical verification) for the baths with a chosen composition and predetermined process performance parameters, the coatings were applied. The Pd content of the coatings (Y_1), and cathodic current efficiency (Y_2) were estimated, then compared with the values computed from the equations. The results are listed in Tables 3 and 4. The comparison proves satisfactory agreement of the computed and measured values.

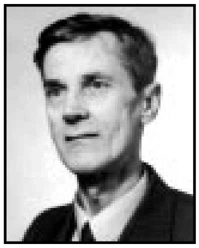
Summary

These researches enabled precise determination of the direction and range of influence of the bath components and process performance parameters on the composition of the Pd-Ni coatings, their microhardness and cathodic current ef-

Table 4
Comparison of Computed And Measured Current Efficiencies For Bath 1 (Table 3)

Current density A/dm^2	Current Efficiency Computed	Current Efficiency Measured
1.0	92.5	92.9
2.0	87.1	87.9
2.5	84.4	84.0
3.0	81.7	79.8

ficiency. Accordingly, it was possible to select the most suitable bath composition and process performance conditions with respect to repeatable deposition of Pd-Ni alloy coatings with 15 to 20 percent Ni content. It is necessary to emphasize that the investigations did not cover the determination of additional material influence on Pd and Ni electroreduction processes. This problem should be subjected to further research, particularly to increase the range of cathodic current densities.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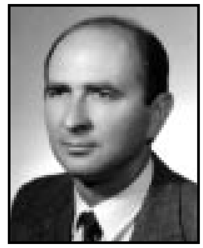
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