Electroless Catalyst Bath Optimization

By N. V. Mandich, CEF

Plating parameters for an electroless plating catalyst system were optimized by use of the fractional test method. Relative **order of importance is established for $PdCl_2$, $SnCi_2$, time, temperature, chloride ion, and PH.**

Electroless plating catalysts are the complex reaction products of palladium chloride and stannous chloride. Commercial catalysts are available either as dry solids or as solutions in hydrochloric acid. Many patents and publications have dealt with the physical and chemical identity of these products.[1-23]

There is little published material on those aspects of a working catalyst bath of real interest to the practicing finisher (i.e., how to get the optimum and most cost-effective catalyst).

Most people regard a supplier-provided catalyst as a "black box." The only changes usually considered are catalyst concentration, immersion time, and sometimes bath temperature.

It is well known that the catalyst synthesis reaction can be influenced by a large number of variables. These include palladium and tin concentrations, the ratio of the two, reaction temperatures and times, hydrogen ion and chloride ion **concentrations, and other factors. This paper** will examine the effects of a number of these same variables on the properties of a catalyst-containing bath.

Six factors were selected for analysis Palladium concentration (expressed as $PdCl_2$), hydrogen ion concentration, chloride ion concentration (in excess of the contribution by $PdCl_2$ and $SnCl_2$), stannous chloride concentration, working bath temperature, and immersion time. The classical testing method consists of varying one factor at a time, while holding all others constant. This is a very tedious **process** when large numbers of variables are being tested. It is also very difficult to locate a multi-variable optimum, and to assign a precise ranking of the magnitude of each effect is difficult also.

An experimental method which eliminates these problems is called the BOX, or Fractional Factorial Test Method. The details of this technique can be found elsewhere.[24-27] Basically, it is a way to analyze and optimize complex mixtures by simultaneously changing all experimental variables in a controlled fashion, in a very small number of experiments. In this case, only eight test baths are necessary to evaluate six different bath variables. A simple mathematical technique serves to analyze the data in terms of the importance of each factor, and to give predictions for preparing optimized solutions. If this same test bath were evaluated in the classical way, using only two different levels for each bath parameter, then 2^6= 64 different test baths would have to be prepared. Even with this number of test baths, only a limited understanding of the effects would result. There would be no easy way to rank each of three variables for optimization of total bath properties. This type of test would be of little use in predicting an optimum formulation.

Experimental Procedure

A commercial, solid, electroless plating catalyst* was used for these tests, with the exception of runs 2 and 3, in which this combination of high palladium and low tin concentrations could not be obtained with the commercial catalyst. A separate low-tin catalyst sample was prepared, using the commercial patented synthesis method for these two runs.

All samples were dissolved in a small volume of reagent-grade HCI. $SnCl_2 \cdot 2H_20$ (95% Sn^{2+}) and KCI were used to adjust Sn^{2+} and Cl- levels. Chloride levels are in addition to that supplied by the palladium and tin salts. Palladium concentration was checked with a UV-visible spectrophotometer after decomposing the **catalyst with peroxide.** Sn^{2+} **and** H+ levels were checked by titration. All catalyst solutions were run in a thermostatically controlled water bath at temperatures held within ±0.55 °C. The times were standardized to ±2 sec.

Test panels were standard EPB-3570-grade ABS.** All panels were etched using 420 g/L CrO_3 and 350 g/L H_2SO_4(93%) for eight min at 15.55 °C. The neutralizer was 12 g/L $NaHSO_3$ for one min at room temperature. The set of panels coated with room-temperature electroless nickel was accelerated **in 120 g/L $NaHS0_4$ + 5% HCI** for 90 sec at 48.88 °C. The panels remained in the nickel bath for only one min. ESCA data have shown that an optimum catalyst layer is completely covered by this room-temperature electroless nickel in 20 to 30 sec. Thus, the nickel film was allowed to develop for only 30 to 40 sac, so that any relationships with the catalyst activity would not be completely obscured. All test panels were thoroughly rinsed in running water after catalysis, then dried. Analyses were done by completely stripping each panel with 3M HCI containing one percent H_20_2. Each of the eight test runs in Table 1 had three separate results for palladium and tin absorption, and for the **amount of nickel deposited in one** min.

Table 1
Fractional Factorial Experiment

	A	B	C	D	E	F
Variable	$PdCl_2$,gL	$H^{\dagger}$,N	Cl^-,N	$SnCl_2$g/L	T,°C	t,min
Base	**0.25**	2.0	2.0	20	28.4	3
Unit	0.15	1.0	1.0	1.0	-9.4	2
High Level	0.40	3.0	3.0	30	37.7	5
Low Level	0.10	1.0	1.0	10	**21.1**	1
Run						
1						
2	+	+	-		+	+
3	+		+		+	
4		+	+			+
5	+			+		+
6		+		+	+	
7			+	+	+	+
8	+	+	+	+		

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* **Dri-Cat 3, Borg-Warner** Chemicals, Melrose Park, IL.
** G.E. **Plastics, Parkersburg, WV.**

Table 2
Analysis of Test Panel Absorption

Run	SnCl$_4$ µg/cm^2	PdCl$_2$ µg/cm^2	Ni, µg/cm^2 at 1 min
1	0.65	0.796	8.76
2	7.17	4.31	52.3
3	9.09	2.85	43.9
4	7.03	2.19	38.0
5	10.40	3.78 ,	50.6
6	9.42	0.863	8.43
7	13.70	1.92	37.3
8	12.10	1.75	42.2

Results

Table 1 shows the experimental test baths. The conditions were selected to encompass commercially usable variations. Each variable was tested at only two distinct levels, high (+) and low (-). Each variable was tested four times at each level. For example, in Run 1, the test bath was used with each variable at its low level. The exact pattern of high and low levels given must be used, as it is distinct for each size of test grid.

Table 2 shows the analyses of the test panels. Note that while each bath variation was relatively minor, their cumulative effects were significant. The absorption of tin varies by a factor of 20, **palladium by a factor of 5, and** nickel by a factor of 6.

Some general correlations can be seen by inspection. Runs 1 and 6 had the lowest palladium absorption, where the immersion times and palladium concentrations were at their minimum values. The amount of usable information obtainable with this approach is limited, however. Detailed analysis of the data can be accomplished by simple calculations. These calculations were done separately for the tin, palladium, and nickel results. This allows the ranking of each bath parameter—not just in relative order of importance-and assignment of hard numerical values for absolute ranking in terms of actual effects.

Table 3 gives the data for tin, nickel and palladium absorption. It is to be expected that palladium absorption should increase with increasing time, temperature, and palladium concentration. The data confirm this and allow quantitative estimation of the relative effects. The results chow that lower values of acidity, chloride, and SnCl$_2$gave better catalyst (palladium) absorption. Acidity has surprisingly little effect; over the range of 1 to 3 M/L, it can be ignored. The SnC1$_2$concentration can be more important than the temperature. It is surprising that palladium absorption is better at lower SnCl$_2$concentrations.

The ranking in order of importance for palladium absorption becomes:

$$PdCl_2 > \text{Time} > SnCl_2 > \text{Temperature} > Cl^- >> H+$$

The nickel results from Table 3 can be similarly interpreted. It was expected that as the palladium absorption increased, the amount of nickel deposited in one min would also increase. Thus, based on the palladium absorbance results, it would be expected that the nickel results would be similar. This was not the case. Only three factors influenced the amount of nickel deposition to any extent. These were palladium concentration, catalyst immersion time and the chloride concentration of the bath. For all three variables, better nickel deposition occurred at greater catalyst concentrations and times. The reason for this is unknown, but it is in direct contrast to the palladium results, in which lower chloride levels increased palladium adsorption. Stannous chloride concentration, catalyst temperature, and bath acidity had essentially no effect on nickel deposition. The rank in order of importance for nickel deposition then is:

$$PdCl_2 > \text{Time} > Cl^- ; SnCl_2 = \text{Temperature} = H^+ = 0$$

The Fractional Factorial analysis has allowed computation of the relative importance of each catalyst bath variable for three different sets of results. This method also allows prediction of an optimized bath formulation. These optimization calculations are a basic part of the Fractional Factorial technique.

Commercial plating operations attempt to optimize catalyst absorption and nickel deposition for greatest cost effectiveness. Nickel deposition depends mainly on palladium concentration and immersion time. The catalyst bath was therefore optimized to promote the absorption of palladium, using the results for nickel deposition in Tables 2 and 3.

Table 4 shows the calculated values for two test baths optimized to give greater catalyst deposition. The standard calculations call for greatly increased palladium concentration and immersion time. This would not be economically acceptable, therefore the calculated parameters were modified. The PdCl$_2$, concentration and the immersion time were kept, as shown in baths Actual I and II, at the original base levels. The values for acidity, chloride, stannous chloride, and temperature were used as calculated. Any changes in absorption **will only be produced by the minor bath variables,** as shown in Table 2.

Bath Actual I showed the highest palladium absorption (5.04 µg) of any test bath. The absorbance was 17 percent greater than for Run 2 from Table 2. Run 2 used a PdCl$_2$concentration 60 percent greater and an immersion time 66 percent greater than run Actual 1. Palladium absorption of Run Actual II (4.52 µg) also exceeded that of Run 2. This shows that the Fractional Factorial method can be used to optimize multi-component plating bathe-possible even when the most “active” component, the reacted tin/palladium catalyst, cannot be changed.

Table 3
Metal Variables and Relative Effect

	Palladium		Tin		Nickel	
	Effect	Rel. Eff.	Effect	Ret. Eff.*	Effect	Rel. Eff.*
PDCI$_2$	+0.865	100	+7.96	37	+12.15	100
H+	-0.03	-3	+1.88	9	+0.05	.004
cL-	-0.13	-15	+14.05	65	+5.16	42
SnCl$_2$	-0.23	-27	+21 .68	100	-0.55	-0.05
Temp.	+0.18	21	+9.20	42	+0.30	0.02
Time	+0.74	77	+7.04	32	+9.36	77

*Based on a scale of 100%

Table 4
Optimal Baths

	A	B	C	D	E	F
	PdCl$_2$	H+	Cl$^-$	SnCl$_2$	Temp °C	Time min
Calculated I	**0.38**	**1.97**	**1.87**	**17.7**	**30,9**	**4.6**
Calculated II	**0.51**	**1.94**	**1.74**	**15.4**	**32.4**	**6.0**
Actual I	**0.25**	**1.97**	**1.87**	**17.7**	**31.1**	3.0
Actual II	**0.25**	**1.94**	**1.74**	**15.4**	**32.2**	**3.0**

Conclusions

The Fractional Factorial Test Method is a useful tool for analysis and optimization of multi-component plating baths. It can **be used both** for ranking each variable or component in order of importance and for mathematically predicting optimized bath parameters to give better results.

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Mandich

About the Author

Ned V. Mandich, CEF, FIMF, is founder, president and research director of HBM Electrochemical & Engineering Co., 2800 Bernice Rd., Lansing, IL 60438. He holds the Dipl. Ing. degree from the University of Belgrade, Yugoslavia; an MS in chemistry from Roosevelt University, Chicago; and is currently a PhD candidate at Aston University, Birmingham, UK. He is chairman of the AESF Hard Chromium Plating Committee.