Use of Experimental Design in the Optimization of Electroplating Solutions

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Experimental design has been around for many years, and with the advent of more powerful desktop computers and user friendly software, this powerful tool is in the hands of bench chemists to optimize electroplating processes.

This paper describes the use of three different experimental design approaches to optimize three plating processes: electroless nickel, semi-bright nickel and trivalent chromium.

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Introduction

The main goal of any experimental design is to minimize the number of experiments, while maximizing the information gleaned. Through careful choice of the model, not only can the main effects of independent experimental variables be determined, but it is also possible to determine if there are interactions between independent variables. This approach contrasts to the classical “one factor at a time” technique, which generally requires significantly more experiments to investigates the same number of variables and misses variable interaction effects entirely.

One of the most important facets of designing an experiment is to lay a solid foundation. This includes defining the purpose of the experiment in terms of important independent and dependent variables.

The “independent” variables (also called factors) are those that will deliberately be controlled at or near predetermined set values. The “dependent variables” (also called responses) are the measured variables whose values are dependent upon the setting of the independent variables.
It pays to know your subject matter. A thorough understanding of the operating parameters and limits will greatly enhance your factor selection and the resulting responses.

It is this information that is vital in determining what type of experimental design one should use.

This paper will discuss three experiments utilizing three different experimental design techniques.

Evaluating the Trivalent Chromium Electrolyte Using a Modified Box-Behnken Design.

Because trivalent chromium processes have been in operation for a number of years, a significant amount of data is available to concerning operating parameters.[1,2] Since there are numerous “independent” variables in a trivalent chromium electrolyte and evaluating all of them would be time consuming and expensive, the available trivalent chromium information was used to choose the most important independent and dependent variables to evaluate.

A modified Box-Behnken design was chosen to evaluate the process. The factors selected were pH, temperature, wetter; Complexor X and Complexor Y. The responses measured were throwing power, efficiency and color. These variables were selected because they are the most critical factors for this process. Table 1 lists the experimental design layout and the results. Table 2 shows the model reduction of the main factors. From this table, it is clear that the main factors that affect throw are: temperature, the squared term of Complexor Y, pH, and the interaction of Complexor X with pH. These values are interpreted from the Prob >F column in Table 2. The smaller the Prob>F value, the greater the effect. Reference 3 goes into more detail about the analysis of variance and the related terms in Table 2.[3]

Figure 1 shows a perturbation plot of the throwing power. The perturbation plot helps one to compare the effect of all the factors at a particular point in the design space. This is accomplished by plotting the response against each factor over its range while holding the other factors constant at their center point.

From Figure 1, the effect of each variable is apparent. For example, at low temperature, the throw is the greatest, and at high temperature, the throw is poorer. Throw or throwing power is the ability to deposit chromium in the low current density area the lower the number the greater the coverage in the low current density area.
Figure 2 shows a plot of temperature versus pH with the other factors held at their midpoint.

From this plot, it is clear that as the temperature decreases, and the pH increases, the throwing power also increases.

The next response evaluated was efficiency. Efficiency is the amount of metal deposited by the current.
Table 3 shows the reduced model of the efficiency design. Because the Adj. R-Squared and Pred R-Squared were too far apart, >0.2, a transformation of the data was required to bring them closer for a better model fit. Transformations are often used to allow the data to better fit the model. In this case the logit transformation that has the equation y' = ln (y – lower/ upper –y) was chosen. Upper and lower are the high and low values respectively.
From Table 3, the efficiency is clearly most affected by Complexor X, the squared term for Complexor Y, and the interaction of Complexor X with pH.
Figure 3 shows the perturbation plot of efficiency.

Figure 4 shows the effects of Compactor X and Complexor Y on efficiency. The efficiency is the maximum when Complexor Y approaches its center point and Complexor X approaches its minimum. As the concentration of Complexor X increases the efficiency decreases. Viewing the data like this shows how the response acts over the range of these factors.

The next response evaluated is color**.** For decorative applications, color of the deposit is an important consideration. Color is very complex phenomenon and is related to the visual perception of tone and hue at various wavelengths of reflected light.[4]

The color of the deposit was measured by a color spectrophotometer. This instrument, frequently used in the paint and coating industry for color formulation, has been useful in quantifying and objectively rating color of the deposit.

The color measurement is the total color difference between hexavalent chromium and trivalent chromium. With a color difference of two (2) it is virtual impossible to tell the coatings apart. Table 4 shows the reduced model of the color experiment. From this model, the main factors that affect color is Complexor X and the squared term of Complexor Y. The main interaction is between Complexor X and pH.
Figure 5 shows the perturbation chart of the effect of the variables on color.

From this chart, it is easy to see the effect of complexor A on color. At low concentration of Complexor A, the color is lighter and at high concentration, the color becomes darker.

Plotting the main factors, it is easier to visualize the interaction of Complexor X and temperature. Figure 6 shows the results.

The next step is to optimize the process. The goal is to obtain the maximum throwing power, the lightest color and a medium efficiency.
The optimization process searches for a combination of factor levels that simultaneously satisfy all of the requirements. Figure 7 shows the results of the optimization of the trivalent chromium process.

The yellow area shows the operating parameters that satisfied the constraints that were put on the model. These constraints were throw less than 30 mm, efficiency between 15-24% and color between 2.9-3.5. The operating parameters defined by these constraints are: temperature between the low value to the center value, complexor Y at the center point, wetter at the high level, complexor X at the low to center point range, and pH at the middle to high range.
Examples of production parts run with the optimized chemistry will be presented in the talk.

Evaluating an Alternative Raw Material Supplier in a Semi-Bright Nickel Process Using a 4-Factor Experimental Design.

The next example will be a semi-bright nickel process. In this example, two different sources of raw material needed to be evaluated. This was set-up as a 4 factor experiment with three factors being the raw materials that are used in the process and the fourth factor a categorical factor. A categorical factor is a non-numeric factor. In this case it was the alternative raw material source.
The design matrix is three levels, -1 0 +1, for the chemicals and two levels for the categorical factor, -1 +1, to differentiate between the two different raw materials. Table 5 shows the experimental design matrix. The response in this experiment are leveling and what I call LCD. When evaluating leveling there was not a significant amount of difference between the two different raw materials. Figure 8 shows the leveling of the two various raw materials.

From this figure the experimental semi-bright nickel had slightly less leveling with low levels of additive 2 and had slightly better leveling with the high level of additive 2 as compared to the standard additive. However, there was not a significant amount of difference in leveling between the two different additives taking into account that there is some over lap in the error bars. Evaluating the leveling at 20 asf, Figure 9, the alternative material had better leveling with low levels of additive. At the high end of additive, the leveling is the same.

The next response looked at called LCD. This is where a significant difference between the two additives can be seen. From Figure 10, the alternative material had significantly lower values for LCD. The higher the LCD value the inferior the deposit. This is magnified with higher levels of additives.

The other significant observation was the leveling in the LCD area. Figure 11 shows the results. From these results, the experimental semi-bright nickel has higher leveling with low levels of additive as compared to the normal semi-bright nickel. However, with high levels of additive the leveling is equivalent.

Using a categorical factor design helps eliminate any bias in evaluating alternative supplier or raw material. In addition, using an experimental design format gives the experimenter a better understanding of the process.

Evaluating a Set of Four Additives in an EN bath using a Central Composite Design.

The next design was a central composite design with four factors and two responsive. The central composite design is composed of a two level full/fractional factorial design, center points and axial points. The central composite design, CCD, can be blocked to run only the factorial points and center points and later run the axial points and center points to further develop the model. For more information on blocking, see reference 5.

Table 6 shows the design layout of the electroless nickel experiment. When you use blocking you would run the factorial and center points of the experiment and analyzes the data. Next, you would run the axial points and center points to finish the experiments in the model. From this, Tables 7 and 8 show the final fit of the CCD data and the fractional part of the data for the rate response respectively. From this the model with all the points had a better fit of the data than the fractional part also the squared term of A and B has an effect on the model. The squared terms can only be deduced by using the axial points in the model. The squared terms are used to fit a quadratic model.

From this work the major interaction was between Additive A and Additive B, Figure 12 shows the results.

From Figure 12 an increase in Additive B increase the rate with low levels of Additive A. As Additive A is increased the rate decrease even with high levels of Additive A.

The next response evaluated was phosphorous content. With the phosphorous results, the axial points did not add any extra value to the analysis of the results.

Figure 13 shows the results of the effect of Additive A vs. Additive B. From this work with low levels of Additive A and B, low phosphorous levels are obtained but with high levels of Additive B and low levels of Additive A higher phosphorous levels are obtained.

Optimizing the electroless nickel process to obtain the highest plating rate while maintaining the phosphorous level above 10% was the next step.

Figure 14 shows the results of the optimization step. From this work, there is a large operating window in which to operate this process to obtain the desired results.

Conclusion:

This work shows that there are various experimental design techniques available for the bench chemist to utilize. Each technique has their own merits and depending on the number of factors and the number of experiments will dictate what model to use. Also, it depends on the amount of time and money you are willing to devote to this process as to what experimental design you will use.

Experimental design does not develop new process it only optimizes and tells what variables have a significant effect on the process.
Instead of 1% inspiration and 99% perspiration for product development, experimental design brings it down to 1% inspiration, 89% perspiration and 10% data entry.

Reference:

1. D.L. Snyder, Plating and Surface Finishing, June 1979, Vol. 66, 60-65

2. D.L. Snyder, product Finishing, December 1990, p 42-48

3. R.H. Myers, D.C. Montgomery, Response Surface Methodology, John Wiley & Sons, 1995

4. Kirk-Othmer Encyclopedia of Chemical Technology 3rd Edition Vol. 6, 523-547

5. G. Box, W. Hunter, J. Hunter, Statistics For Experimenters John Wiley & Sons, 1978

Table 1

Std.	Run #	Block	Complexor X	pH	Temp (°F)	Complexor Y	Wetter	Throw	Efficiency	Color
17	1	1	0	0	1	0	-1	35	20.7	3.6
22	2	1	1	0	0	-1	1	40	6.7	3.78
16	3	1	0	1	0	0	-1	18	11.9	4.46
11	4	1	1	0	1	0	1	38	13.2	3.26
15	5	1	0	-1	1	0	1	40	14.9	3.61
14	6	1	0	0	0	0	1	24	22.2	2.76
10	7	1	1	0	0	0	-1	16	9.8	8.74
12	8	1	-1	0	1	0	1	24	25.8	1.91
21	9	1	0	-1	0	0	-1	28	17	3.54
23	10	1	0	0	0	0	1	15	21.4	3.8
18	11	1	-1	1	0	0	1	16	22.4	3.07
9	12	1	-1	0	0	1	1	25	18.6	4.16
1	13	1	0	1	1	0	1	33	23.5	2.73
20	14	1	-1	-1	0	0	1	18	25.8	3.29
13	15	1	0	0	1	1	1	52	2	3.92
19	16	1	0	0	0	1	-1	25	20.9	3.21
2	17	1	-1	0	0	0	-1	18	24.5	2.98
24	18	1	-1	0	0	-1	1	22	22.7	3.8
26	19	1	1	0	0	1	1	45	3.9	8.61
3	20	1	0	1	0	1	1	32	12.8	6.08
8	21	1	1	1	0	0	1	14	17.5	3.41
7	22	1	0	0	1	-1	1	42	5.4	2.43
6	23	1	0	0	0	0	1	20	18.8	3.23
25	24	1	0	0	0	-1	-1	17	13.1	7.08
5	25	1	1	-1	0	0	1	43	1.9	4.7
4	26	1	0	0	0	0	1	18	22	4.01

Table 2

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	2801.820	9.000	311.313	17.642	< 0.0001
A	70.417	1.000	70.417	3.990	0.0631
B	312.667	1.000	312.667	17.719	0.0007
C	991.512	1.000	991.512	56.189	< 0.0001
D	91.181	1.000	91.181	5.167	0.0372
E	59.031	1.000	59.031	3.345	0.0861
B2	78.355	1.000	78.355	4.440	0.0512
D2	613.883	1.000	613.883	34.789	< 0.0001
AB	182.250	1.000	182.250	10.328	0.0054
AE	120.417	1.000	120.417	6.824	0.0189
Residual	282.338	16.000	17.646		
Lack of Fit	239.588	13.000	18.430	1.293	0.4706
Pure Error	42.750	3.000	14.250		
Cor Total	3084.150	25.000			

Std. Dev.	4.201	R-Squared	0.908
Mean	27.615	Adj R-Squared	0.857
C.V.	15.212	Pred R-Squared	0.758
PRESS	744.931	Adeq Precision	13.179

Table 3 Efficiency Reduced Model

ANOVA for Response Surface Reduced Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	52.551	5.000	10.510	11.908	< 0.0001
A	31.504	1.000	31.504	35.695	< 0.0001
B	1.497	1.000	1.497	1.696	0.2077
D	0.416	1.000	0.416	0.471	0.5004
D2	12.109	1.000	12.109	13.720	0.0014
AB	7.351	1.000	7.351	8.329	0.0091
Residual	17.652	20.000	0.883		
Lack of Fit	17.320	17.000	1.019	9.205	0.0461
Pure Error	0.332	3.000	0.111		
Cor Total	70.203	25.000			

Std. Dev.	0.939	R-Squared	0.749
Mean	0.423	Adj R-Squared	0.686
C.V.	221.985	Pred R-Squared	0.575
PRESS	29.826	Adeq Precision	13.188

Table 4 Color Reduced Model

ANOVA for Response Surface Reduced Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	52.551	5.000	10.510	11.908	< 0.0001
A	31.504	1.000	31.504	35.695	< 0.0001
B	1.497	1.000	1.497	1.696	0.2077
D	0.416	1.000	0.416	0.471	0.5004
D2	12.109	1.000	12.109	13.720	0.0014
AB	7.351	1.000	7.351	8.329	0.0091
Residual	17.652	20.000	0.883		
Lack of Fit	17.320	17.000	1.019	9.205	0.0461
Pure Error	0.332	3.000	0.111		
Cor Total	70.203	25.000			

Std. Dev.	0.939	R-Squared	0.749
Mean	0.423	Adj R-Squared	0.686
C.V.	221.985	Pred R-Squared	0.575
PRESS	29.826	Adeq Precision	13.188

Table 5 Design Matrix for Semi-bright Nickel

Std.	run	Block	A	B	C	D
5	4	{ 1 }	-1	0	-1	{ -1 }
19	5	{ 1 }	1	-1	-1	{ 1 }
2	6	{ 1 }	0	1	-1	{ -1 }
4	7	{ 1 }	1	-1	1	{ -1 }
23	8	{ 1 }	-1	1	1	{ -1 }
14	9	{ 1 }	-1	-1	0	{ -1 }
1	10	{ 1 }	1	1	1	{ 1 }
7	11	{ 1 }	-1	-1	-1	{ 1 }
24	12	{ 1 }	1	1	0	{ -1 }
13	13	{ 1 }	-1	-1	1	{ 1 }
22	14	{ 1 }	-1	1	0	{ 1 }
6	15	{ 1 }	1	1	-1	{ 1 }
21	16	{ 1 }	1	1	-1	{ 1 }
12	17	{ 1 }	0	0	-0.5	{ 1 }
16	18	{ 1 }	-0.5	0	0.5	{ 1 }
3	19	{ 1 }	1	1	0	{ -1 }
15	20	{ 1 }	0	0	0.5	{ -1 }
11	21	{ 1 }	-1	1	1	{ -1 }
18	22	{ 1 }	-1	-1	-1	{ -1 }
20	23	{ 1 }	0	1	-1	{ -1 }
8	24	{ 1 }	-1	1	0	{ 1 }

Table 6 Central Composite Design of Electroless Nickel

Std.	Run	Block Type	Additive A	Additive B	Additive C	Additive D	Rate (mils/Hr)	%P
3	1	Fact	15.00	25.00	2.50	2.50	0.63	10.13
2	2	Fact	25.00	15.00	2.50	2.50	0.53	11.00
11	3	Fact	15.00	25.00	2.50	7.50	0.57	10.65
8	4	Fact	25.00	25.00	7.50	2.50	0.53	11.14
25	5	Center	20.00	20.00	5.00	5.00	0.54	10.50
10	6	Fact	25.00	15.00	2.50	7.50	0.60	11.50
16	7	Fact	25.00	25.00	7.50	7.50	0.54	10.50
12	8	Fact	25.00	25.00	2.50	7.50	0.58	10.14
19	9	Axial	20.00	10.00	5.00	5.00	0.53	10.50
4	10	Fact	25.00	25.00	2.50	2.50	0.46	10.20
1	11	Fact	15.00	15.00	2.50	2.50	0.56	10.47
18	12	Axial	30.00	20.00	5.00	5.00	0.50	10.20
22	13	Axial	20.00	20.00	10.00	5.00	0.60	10.25
17	14	Axial	10.00	20.00	5.00	5.00	0.70	9.34
7	15	Fact	15.00	25.00	7.50	2.50	0.61	9.90
24	16	Axial	20.00	20.00	5.00	10.00	0.61	9.48
15	17	Fact	15.00	25.00	7.50	7.50	0.74	9.58
6	18	Fact	25.00	15.00	7.50	2.50	0.52	10.00
27	19	Center	20.00	20.00	5.00	5.00	0.58	9.80
21	20	Axial	20.00	20.00	0.00	5.00	0.57	10.50

Std.	Run	Block Type	Additive A	Additive B	Additive C	Additive D	Rate (mils/Hr)	%P
14	21	Fact	25.00	15.00	7.50	7.50	0.56	9.30
5	22	Fact	15.00	15.00	7.50	2.50	0.49	9.00
13	23	Fact	15.00	15.00	7.50	7.50	0.66	9.18
9	24	Fact	15.00	15.00	2.50	7.50	0.57	9.76
23	25	Axial	20.00	20.00	5.00	0.00	0.48	10.45
20	26	Axial	20.00	30.00	5.00	5.00	0.58	10.20
26	27	Center	20.00	20.00	5.00	5.00	0.56	10.15
28	28	Fact	15.00	25.00	2.50	7.50	0.58	10.70

Table 7 ANOVA for CCD Design.

Std. Dev.	0.017	R-Squared	0.963
Mean	0.571	Adj R-Squared	0.923
C.V.	2.975	Pred R-Squared	0.775
PRESS	0.023	Adeq Precision	21.968

Table 8 ANOVA for Factorial part of CCD Design.

Std. Dev.	0.027	R-Squared	0.906
Mean	0.574	Adj R-Squared	0.812
C.V.	4.747	Pred R-Squared	0.642
PRESS	0.026	Adeq Precision	13.585

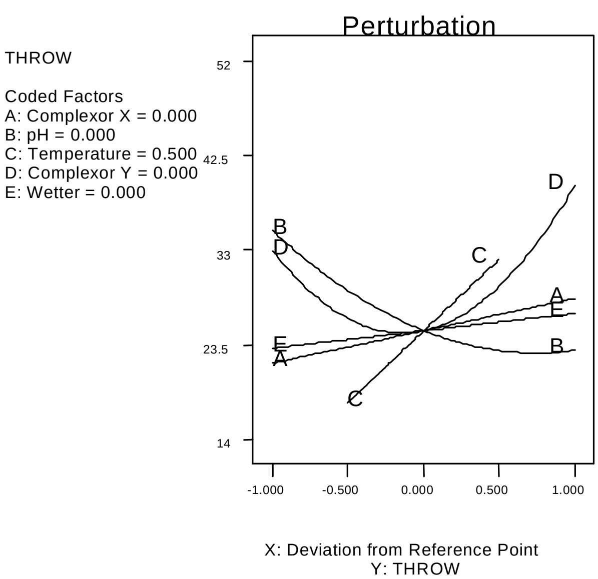

Figure 1 Perturbation Chart of Throw

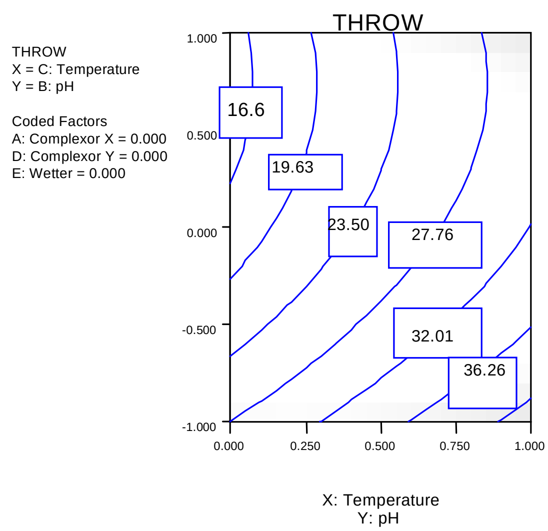

Figure 2 Effect of Temperature vs pH on Throw

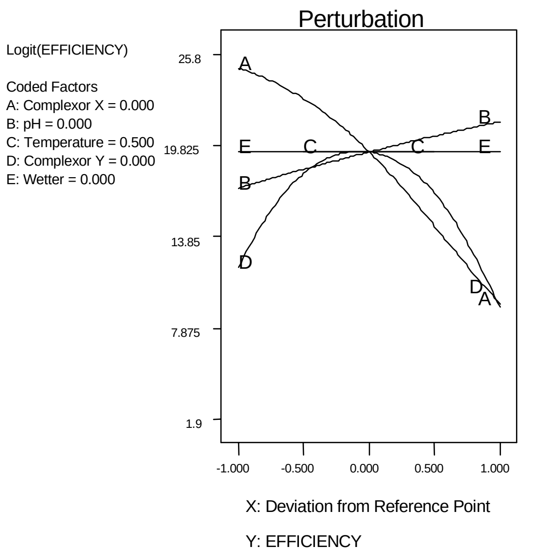

Figure 3 Perturbation Plot of Efficiency

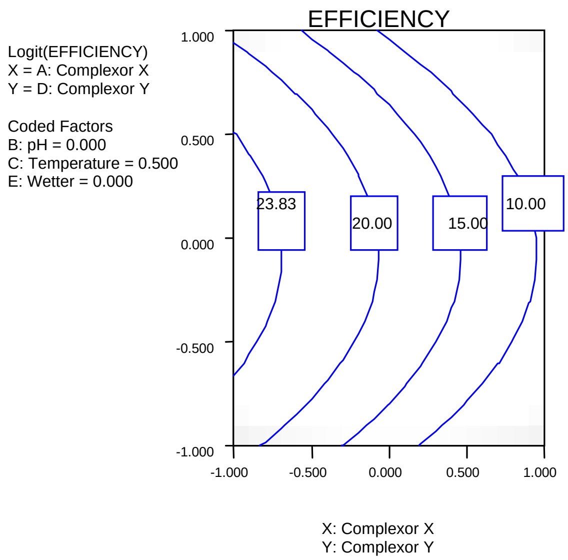

Figure 4 Effect of Complexor X vs. Complexor Y on Efficiency

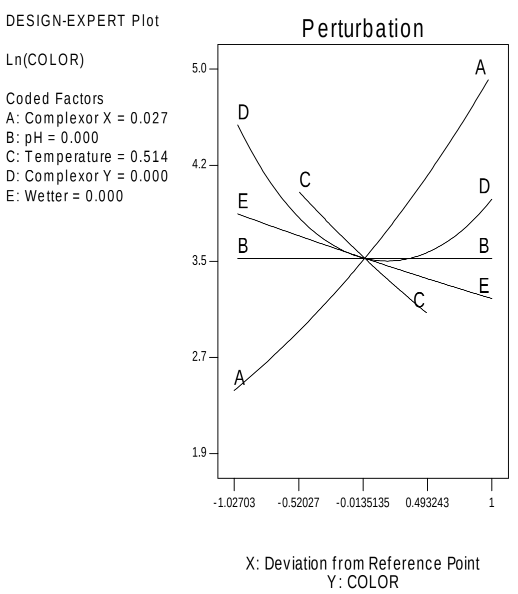

Figure 5 Perturbation Chart of Color

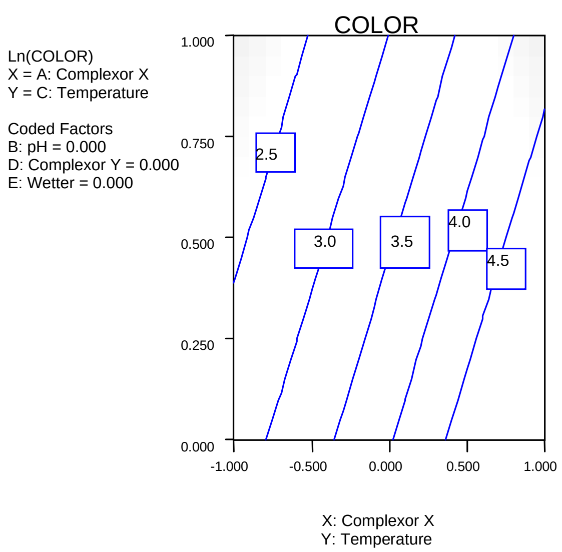

Figure 6 Effect of Temperature and Complexor X on Color.

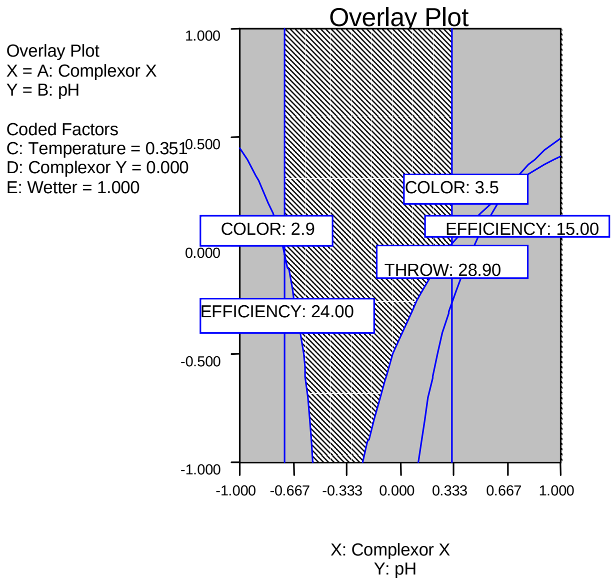

Figure 7 Optimization of Trivalent chromium process.

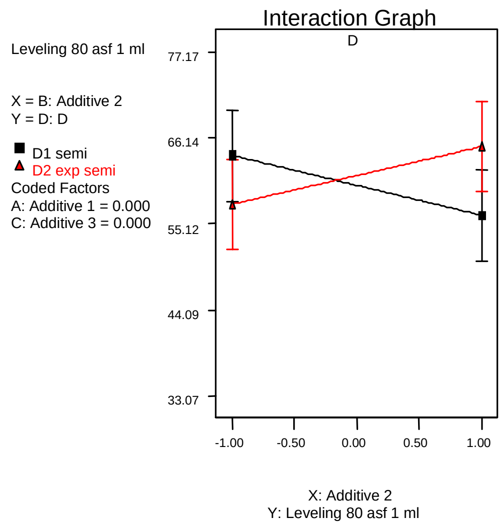

Figure 8 Leveling @ 80 ASF.

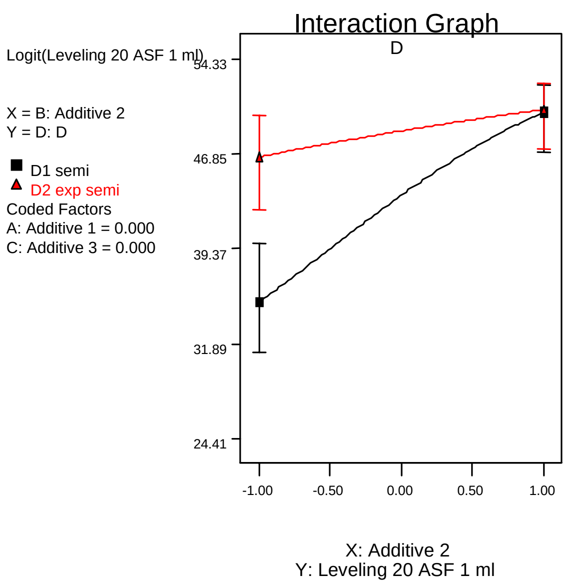

Figure 9 Leveling at 20ASF

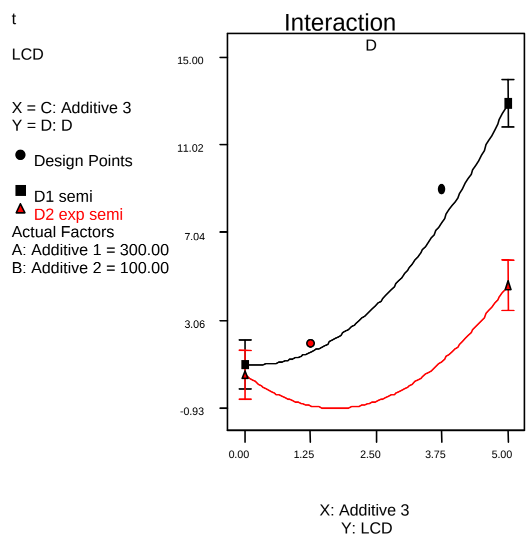

Figure 10 LCD values verses Additive

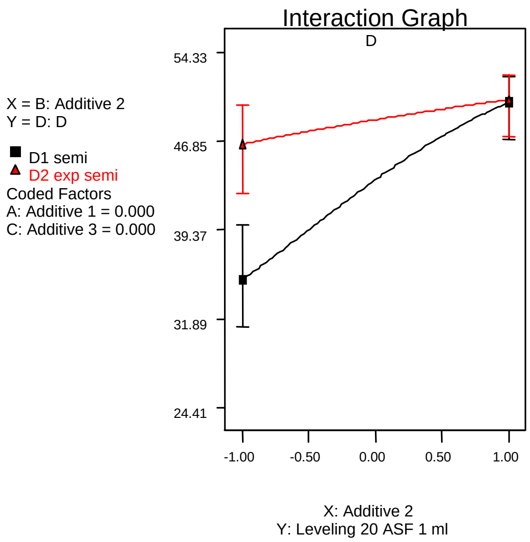

Figure 11 Leveling at 20 ASF

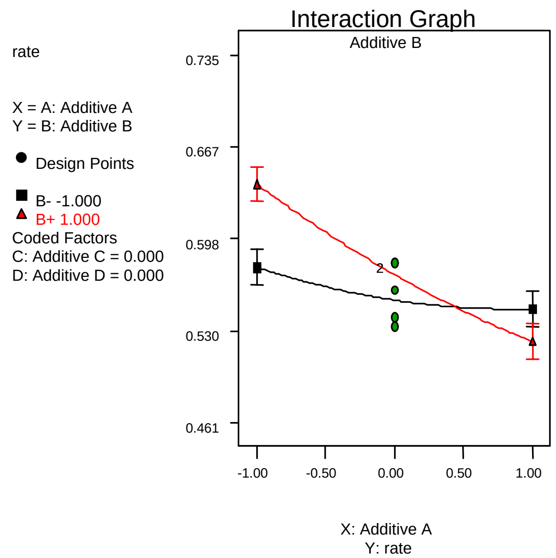

Figure 12 Effect of Rate by Additive A and B.

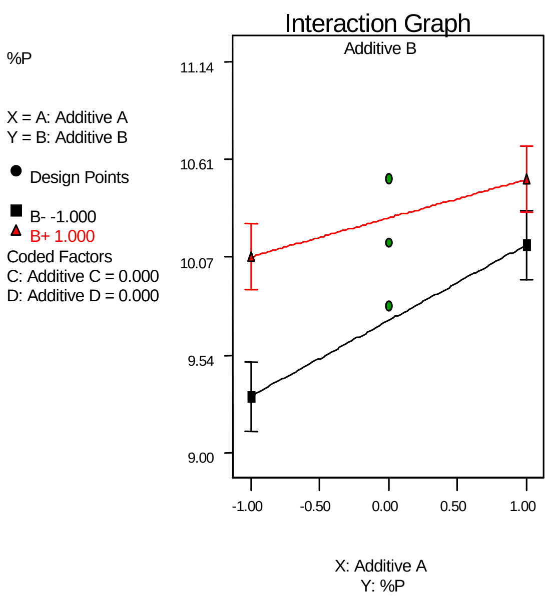

Figure 13 Effect of Additive A and B on Phosphorous.

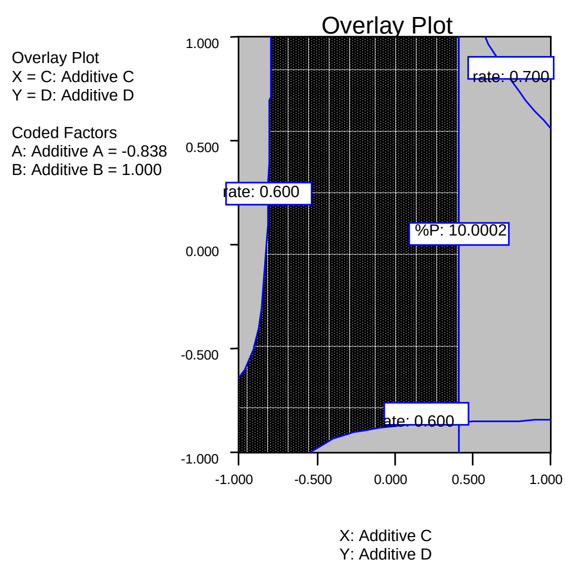

Figure 14 Optimization of Electroless Nickel Process.