The Effect of Additives on the Internal Stress Of Nickel Deposits from Watts Baths

By Shih-Min Lin and *Ten-Chin* Wen

For minimizing stress, the optimum concentrations of Class I and Class II brighteners and a surfactant in a Watts bath were determined by measuring the curl of thin strips plated with nickel and using orthogonal array techniques and statistical analysis. The optimum concentrations were 0.72 g/L saccharin; 0.17 g/L 2-butyne-1,4 diol; and 0.60 g/L aerosol AY.

Nickel electroplate is used for decorative, engineering and electroforming purposes because its appearance and properties can be controlled and varied over broad ranges.[1,2] Water-soluble organic compounds are added to control desired properties.[3,4] Compounds commonly added to Watts baths are brighteners that fall into two classes;[5] 2-butyne-1,4 diol (BD) is a class II brightener’ that is still popular after more than 20 years of use. It results, however, in large tensile stress in the deposit. Class 1 brighteners such as saccharin (SA), naphthalene-1 ,5-disulfonate disodium (NDS) and naphthalene trisulfonate (NTS) have been used as stress reducing agents in Watts baths that contain BD. These agents contribute sulfur to the deposit.’ The importance of minimizing stress is well recognized.[8] Stress ranges from 0 to 55 MPa and 125 to 186 MPa in deposits from sulfamate and Watts nickel baths, respectively. Although sulfamate solutions are most commonly used for electroforming, there is a problem with oxidation of sulfamate ions, particularly at high temperatures and low pH.

Watts baths with an appropriate stress- reducing agent are still competitive. Huang studied the stress-reducing effects of class I brighteners, including 23 sulfonates.[4] The study of organic additives in Watts baths has been conducted by varying one factor at a time, with the remaining factors held constant. This method was once regarded as the correct research procedure, but is appropriate only if all factors act independently. When the factors interact, the results of this one-factor-at-a-time design may be misleading.[9,10]

An efficient procedure for studying the effect of organic additives on stress in bright nickel deposits is presented in this paper. To validate the procedure, the orthogonal array method[9,10] advocated by Genichi Taguchi was applied in designing the experiments. The experimental plans adopted are called orthogonal arrays because they permit estimation of all main effects of a factorial arrangement without correlation. At the same time, interactions can be assigned by using a grouping scheme from Abelian group theory. The most commonly and easily used orthogonal arrays involve factors that occur with the same number of levels, such as two and three levels, which were applied in our study. The calculations from data analysis of the orthogonal arrays are listed in the Appendix. To find the settings of the experimental factors that produce the real minimum stress value, response surface” procedures, with another efficient experimental design (Central Composite Design), were used with additional experiments and regression analysis.

Experimental Procedure

A distilled water bath containing 250 g/L $NiSO_4 \cdot 6H_20$, 40 g/L $NiCl_2 . 6H_20$ and 35 g/L H_3BO_3 was adopted. A wetting agent, aerosol AY,* was added to inhibit pitting; its critical concentration in a sulfamate solution was reported to be about 0.2 g/L.[12] A thin-strip method involving 25.4 pm-thick, copper foils was used to determine internal stress. The stress of the copper foils was released by heating with a household iron. The foils were degreased with soapy water, rinsed in distilled water, acid-cleaned in 10-percent hydrochloric acid solution and rinsed with distilled water.

Cleaned copper foils were plated in a Hull cell at 2 A in a bath with a temperature of 55 °C. The degree of curl at the high current density end of the foil was indicative of the stress, which was quantitatively correlated with spiral contractometer measurements by Huang.[3] The thin-strip method was preferred for this study because it is simpler than that involving the spiral contractometer. The degree of curl of the plated copper foils was measured three times with an angle gage and the mean values were used to generate the analysis of variance for the statistical inference.

Results and Discussion

Class I brighteners SA, NDS and NTS, and class II brightener BD, were adopted with aerosol AY for a two-level experimental design. The designed factors and concentrations for 16 experiments in a $L_{16}(2^{15})$ array are listed in Table 1. The foil-curl values shown in Table 2 were used to generate analysis-of-variance. From the values of F in Table 3, NDS, NDS and

Table 1
Factors and Levels for Array $L_{16}(2^{15})$

Factor	Concentration, g/L Level 1	Level 2
BD	0.2	0.4
SA	0.2	0.4
AY	0.4	0.8
NDS	0.2	0.4
NTS	0.2	0.4

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*Lutensit ARP, BASF Corp.

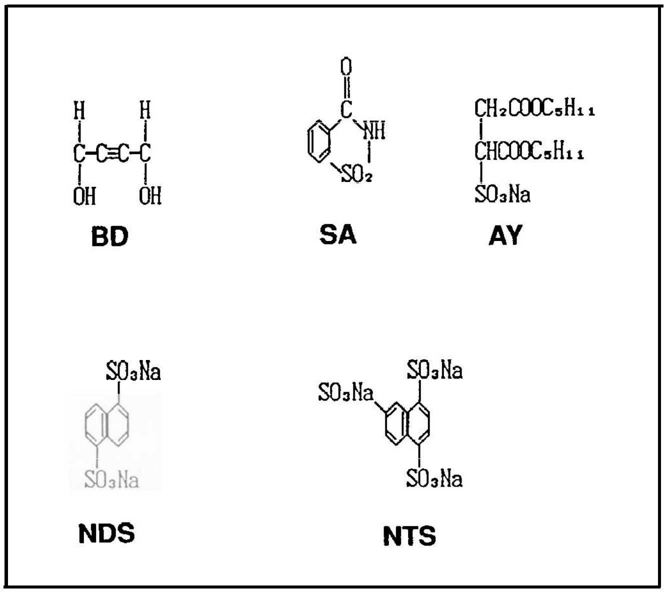

Fig. 1—Molecular structure of addition agents.

Table 2
Experimental Data for Array $L_{16}(2^{15})$

Exp. No.	Concentration, g/L BD	SA	AY	NDS	NTS	Curl, degrees
1	0.2	0.2	0.4	0.2	0.2	9
2	0.2	0.2	0.4	0.4	0.4	11
3	0.2	0.2	0.8	0.2	0.4	10
4	0.2	0.2	0.8	0.4	0.2	10
5	0.2	0.4	0.4	0.2	0.4	2
6	0.2	0.4	0.4	0.4	0.2	2
7	0.2	0.4	0.8	0.2	0.2	5
8	0.2	0.4	0.8	0.4	0.4	-3
9	0.4	0.2	0.4	0.2	0.4	50
10	0.4	0.2	0.4	0.4	0.2	63
11	0.4	0.2	0.8	0.2	0.2	85
12	0.4	0.2	0.8	0.4	0.4	68
13	0.4	0.4	0.4	0.2	0.2	45
14	0.4	0.4	0.4	0.4	0.4	35
15	0.4	0.4	0.8	0.2	0.4	45
16	0.4	0.4	0.8	0.4	0.2	30

aerosol AY can be inferred to have less effect on stress than BD and SA.

The molecular structures of the organic additives are shown in Fig. 1. Only BD, which promotes high stress, is not a sulfur-containing compound. In SA, sulfur is enclosed in a ring and is a part of a SO_2 group, but exists in a disassociated SO_3Na group in the other additives. Although additives that contribute sulfur to the deposit are effective stress reducers, the resultant deposits are susceptible to embrittlement when heated to a temperature above 200 °C. The brittleness of such deposits can be avoided by adding manganous sulfate to the plating bath and codepositing manganese.[13]

From a chemical viewpoint, the reduction of sulfur in the SO_2 group to the sulfide ion should be much easier, by comparison with its reduction from the SO_3Na group, because the sulfur atom is surrounded by more negative electrons in the SO_3Na group. This expectation is consistent with the results given in Table 2. However, the results of the effects of NDS and NTS on the reduction of stress are not consistent with previous literature reports? The results of determining stress while organic additives are added simultaneously are much different from the data obtained with the one-at-a-time method. It now appears that the reduction of sulfur in the SO_2 group is actually easier than the reduction of sulfur in the SO_3Na group, thereby producing sulfide ions that contribute sulfur to the deposit.

Additional experiments were undertaken to develop a better understanding of the effects of BD, SA and the interaction between them; 27 experiments in a $L_{27}(3^{13})$ array were made for further statistical analysis. The designed conditions and

Table 3
Analysis of Variance for Array $L_{16}(2^{15})$

Source	Sum of squares	Freedom degrees	Mean square	F
BD	8789.06	1	8789.06	125.95**
SA	1314.06	1	1314.06	18.83*
AY	68.06	1	68.06	0.98
NDS	76.56	1	76.56	1.10
NTS	60.06	1	60.06	0.88
BD+SA	370.06	1	370.56	5.31*
Error	628.06	9	69.78	

● Significant
**Very significant

Table 4
Factors and Levels for Array $L_{27}(3^{13})$

Factor	Concentration, g/L Level 1	Level 2	Level 3
BD	0.2	0.4	0.8
SA	0.2	0.4	0.8
AY	0.4	0.8	1.6

Table 5
Experimental Data for Array $L_{27}(3^{13})$

Exp.	Concentrate ion g/L SA	BD	AY	Curl, degrees
1	0.2	0.2	0.4	20
2	0.2	0.2	0.8	18
3	0.2	0.2	1.6	16
4	0.2	0.4	0.4	61
5	0.2	0.4	0.8	35
6	0.2	0.4	1.6	30
7	0.2	0.8	0.4	360
8	0.2	0.8	0.8	320
9	0.2	0.8	1.6	270
10	0.4	0.2	0.4	15
11	0.4	0.2	0.8	10
12	0.4	0.2	1.6	0
13	0.4	0.4	0.4	62
14	0.4	0.4	0.8	50
15	0.4	0.4	1.6	30
16	0.4	0.8	0.4	180
17	0.4	0.8	0.8	120
18	0.4	0.8	1.6	100
19	0.8	0.2	0.4	-2
20	0.8	0.2	0.8	0
21	0.8	0.2	1.6	-2
22	0.8	0.4	0.4	50
23	0.8	0.4	0.8	25
24	0.8	0.4	1.6	30
25	0.8	0.8	0.4	270
26	0.8	0.8	0.8	180
27	0.8	0.8	1.6	100

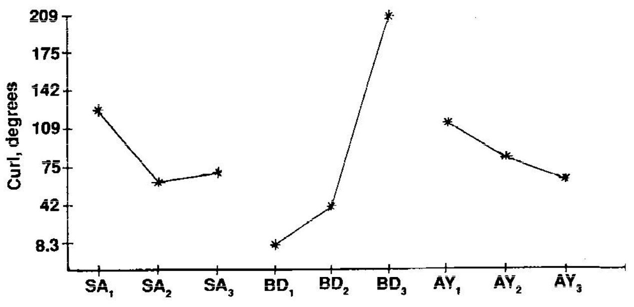

Fig. 2—The curl of copper toll at different levels of SA, BD and AY. Sub-Scripts represent additive levels.

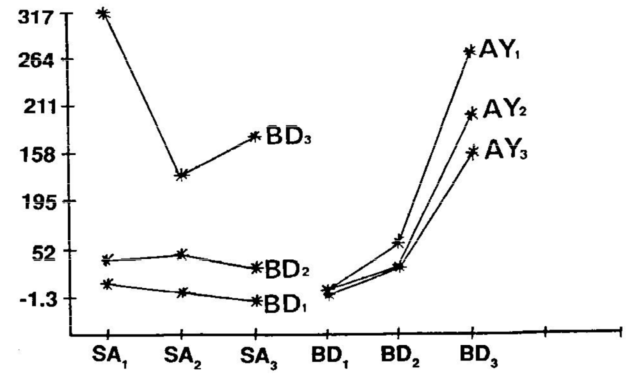

Fig. 3-The effect of the interactions of BD and SA end of BD end AY of the curl of copper foll. Subscripts represent additive levels.

corresponding results are shown in Tables 4 and 5, respectively. The analysis of variance computed from the experimental data is given in Table 6.

Figure 2 indicates that brightener BD has a much greater effect on tensile stress than SA or aerosol AY has on compressive stress. Brightener BD, which has an unsaturated bond and two OH groups that are absorbed at the cathode, refines the grain size of the nickel deposit and possibly causes crystal dislocations. Class I brightener SA has an aromatic structure and the $S0_2$ group that contributes considerable sulfur and consequently reduces stress. Surfactant aerosol AY also has a slight effect on the reduction of stress, as a result of its SO_3Na group. The results are consistent with the F values in Table 6.

Figure 3 shows the effects of interactions between BD and SA and those between BD and AY. The greatest interaction occurs with the highest concentration of BD and any of the SA levels.

Table 6
Analysis of Variance for Array $L_{27}(3^{13})$

Source	Sum of squares	Freedom degrees	Mean square	F
SA	21113.55	2	10556.78	42.0*
BD	208069.56	2	304034.78	413.9**
AY	11094.22	2	5547.11	22.1 *
BD+SA	34765.55	4	8691.39	34.58*
BD+AY	9843.55	4	2460.89	9.80”
Error	3016.19	12	251.35	

*Significant
**Very significant

Table 7
Factors and Levels for Central Composite Design

Agent	Concentration, g/L Level 1 (-1)	Level 2 (+1)	Center Point (o)
SA	0.4	0.8	0.6
BD	0.2	0.4	0.3
AY	0.4	0.8	0.6

An analysis of the data generated can identify the optimum additive concentrations for minimizing stress. From Table 5, deposits 12 and 20 showed the least foil-curl. By using a statistical inference procedure (Appendix) and the data in Fig. 2, the point estimation for experiment 12 is-19.11 and its 95 percent confidence level is 17.59. Therefore, its range spans -1.52 to -36.7 degrees of foil-curl and does not overlap zero stress. On the other hand, the prediction for deposit 20 ranges from -29.59 to 5.59 degrees and can be accepted as defining the optimum conditions for stress minimization. Thus, a combination of 0.8 g/L of SA, 0.2 g/L of BD and 0.8 g/L of aerosol in the Watts bath is considered to be optimum, on the basis of our study.

Although the optimum brightener concentrations given above were confirmed three separate times, we looked for further verification. Therefore, response surface procedures were used next. First, a linear model was assumed and four experiments shown in Table 7 were made up for linear regression, which generated analysis-of-variance given in Table 8 and the coefficients of the equation:

$$CD= 19.08- 8(SA) + 20.5(BD)-5(AY) \qquad (1)$$

where CD designates the curl in degrees. Based on the F and R^2values in Table 9, it was concluded that the linear regression model was unsuitable for a correlation of internal stress. Thus,

Table 8
Experimental Data for Linear Analysis

Exp. No.	SA Level	BD Level	AY Level	Curl, degrees
10	-1	-1	-1	15
11	-1	-1	1	10
13	-1	1	1	62
14	-1	1	1	50
19	1	-1	-1	-2
20	1	-1	1	50
22	1	1	-1	20
23	1	1	1	5
28*	0	0	0	-8
29*	o	0	0	11
30*	o	0	0	0
31”	0	0	0	4

‘New experiments

Table 9
Analysis of Variance for Linear Regression

Source	Sum of squares	Freedom degrees	Mean square	F
Total	5580.92	11		
Regression	4074.00	3	1358.00	84.92
Lack of fit	1444.17	5	288.83	13.80
Pure error	62.75	3	20.92	

$R^2 = 0.73$

a quadratic form was adopted. Six experiments shown in Table 10 were then conducted. Computations showed regression coefficients, as follows:

$$CD = \qquad (2)$$

$$18.39 - 8.38(SA) + 19.4(BD) - 4.41(AY) + 5.46(SA)^2 + 7.23(BD)^2 + 5.81(AY)^2 - 1.25(SA)(BD) - 0.75(SA)(AY) - 4.25(BD)(AY)$$

The computations also showed the analysis of variance in Table 11. Based on the F and R^2 values, it was concluded that the quadratic form was a good model for determining stress in terms of degrees of curl. The magnitudes of the coefficients indicate that the concentrations of BD and SA have a greater effect on curl degrees than those of AY. For convenience in calculating the optimum concentrations for stress minimization, Eq. (2) can be transformed to the canonical form:

$$CD = 3.34 + 3.98(W_1)^2 + 5.73(W_2)^2 + 8.79(W_3)^2, \qquad (3)$$

where

$$W_1 = 0.42(SA - 0.61) + 0.53(BD + 1.3) + 0.72(AY + 0.06),$$

$$W_2 = 0.91(SA - 0.61) - 0.17(BD + 1.3) - 0.38(AY + 0.06),$$

$$W_3 . \; 0.09(SA - 0.61) - 0.82(BD + 1.3) + 0.57(AY + 0.06)$$

The optimum concentrations obtained when W_1, W_2 and W_3 are equal to zero are: SA=0.72 g/L, BD=0.17 g/L and AY = 0.60 g/L.

Table 11
Analysis of Variance for the Fit of Quadratic Form

Source	Sum of squares	Freedom degrees	Mean square	F
Total	7848.28	17		
Regression	7571.54	9	841.28	40.22
Lack of fit	313.98	5	62.79	3.0
Pure error	62.75	3	20.92	

$R^2 = 0.95$

Table 10
Experiments by Central Composite Design for the Fit of Quadratic Form

Exp. No.	SA	BD	AY	Curl, degrees
32	1.6818	0	0	0
33	-1.6818	0	0	30
34	0	1.6818	0	50
35	0	-1.6818	0	-10
36	0	0	1.8818	10
37	0	0	-1.6818	22

Conclusions

The orthogonal array method was shown to be useful for studying the effect of additives on the internal stress of Watts nickel deposits. The thin-strip method was validated as a simple, valuable tool for measuring stress. Our data show that naphthalene-1 ,5-disulfonate disodium and naphthalene trisulfonate have less effect on reducing stress than saccharin, which has a different sulfur-containing group. Saccharin has less effect on reducing stress than 2-butyne-1,4 diol has on increasing stress. The interactive effects of the additives on stress can be established by statistical analysis. Surface response procedures are effective for determining optimum additive concentrations or defining a region of input variables where certain operating specifications can be established. The real optimum additive concentrations for minimum stress in Watts nickel deposits, which were identified by surface response procedures, were found to be 0.72 @l-saccharin, 0.17 g/L 2-butyne-1,4 diol and 0.60 g/L of aerosol AY.

Appendix

Orthogonal arrays can be traced to Euler's Graeco-Latin squares. The idea of using orthogonal arrays for designing experiments was studied in the United States and Japan during World War II. Later, studies on orthogonal functions corresponding to orthogonal arrays were conducted for assigning experiments in the case of a two-level system.

In general, the most commonly used orthogonal arrays involve factors that all occur with the same number of levels, such as two-level systems: $L_4(2^3)$, $L_8(2^7)$, $L_{16}(2^{15})$ and $L_{32}(2^{31})$ or three-level systems: $L_9(3^4)$, $L_{27}(3^{13})$ and $L_{81}(3^{40})$. Table A1 de-

Table A1
$L_{16}(2^{15})$ Orthogonal Array

Exp.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2
3	1	1	1	2	2	2	2	1	1	1	1	2	2	2	2
4	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1
5	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2
6	1	2	2	1	1	2	2	2	2	1	1	2	2	1	1
7	1	2	2	2	2	1	1	1	1	2	2	2	2	1	1
8	1	2	2	2	2	1	1	2	2	1	1	1	1	2	2
9	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
10	2	1	2	1	2	1	2	2	1	2	1	2	1	2	1
11	2	1	2	2	1	2	1	1	2	1	2	2	1	2	1
12	2	1	2	2	1	2	1	2	1	2	1	1	2	1	2
13	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1
14	2	2	1	1	2	2	1	2	1	1	2	2	1	1	2
15	2	2	1	2	1	1	2	1	2	2	1	2	1	1	2
16	2	2	1	2	1	1	2	2	1	1	2	1	2	2	1

Table A2
$L_{27}(3^{13})$ Orthogonal Array

Exp.	A	B	C	D	E	F	G	H	I	J	K	L	M
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	1	2	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

scribes the design conditions of the $L_{16}(2^{15})$array applied in our study. The $L_{27}(3^{13})$arraywe also used is shown in Table A2.

To construct the analysis of variance table, the sum of squares of the controlled factors for $L_{16}(2^{15})$ was calculated as follows:

$$SS_i = (\Sigma y_{1j} - \Sigma y_{2j})^2/16$$

where subscript i = 1 to15 factors (including main effects and interactions) and subscript j represents level 1 or 2. An example for the first column is:

$$SS_i =$$

$$(y_1+y_2+y_3+y_4+y_5+y_6+y_7+y_8-y_9-y_{10}-y_{11}-y_{12}-y_{13}-y_{14}-y_{15}-y_{16})^2/16$$

The sum of squares for $L_{27}(3^{13})$ was calculated as follows:

$$SS_i =$$

$$[(\Sigma y_{1j})^2 + (\Sigma y_{2j})^2 + (\Sigma y_{3j})^2]/9 - (\Sigma y_{1j} + \Sigma y_{2j} + \Sigma y_{3j})^2/27$$

To test the null hypothesis from the analysis-of-variance, the test statistic is F = MSA/MSE,where MSA is the treatment mean square of factor A, obtained by dividing the sum of squares (SS) with the number of degrees of freedom (df) and the [(number of levels) -1]. MSE is the mean square error from the analysis of variance. If calculated F is greater than table F (r_1, r_2, α), the effect is said to be significant at a 100-α-percent significance level, where r_1 and r_2 are the degrees of freedom of controlled factors and error, respectively. $F(r_1,r_2,\alpha)$ is the F value at a probability level.

Acknowledgment

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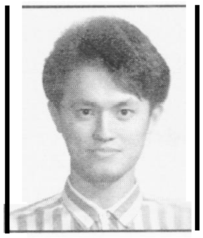

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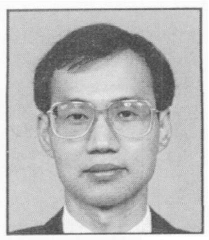

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