Influence of Commercial Organic Additives on the Nickel Electroplating

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This study investigated the combined effects of commercial electroplating additives on the properties of nickel electrodeposits. Pieces of carbon steel were electroplated in a Hull cell, using the Watt's bath with different concentrations of additives and different times of deposition according a 25-1 fractional factorial design. Three response variables, namely brightness, roughness and charge transfer resistance were studied. Several synergistic and antagonistic interactions between the studied factors were found and briefly discussed on a physical basis. Principal Component Analysis (PCA) revealed that clustering in PC-space can be associated with morphological characteristics of the coatings.

1. INTRODUCTION

Organic additives have been used in the electroplating industry for many years. All electroplating baths have additives in their formulation, applied with different purposes such as leveling, grain refinement and decreasing of internal stress. The industrial organic additives formulation has evolved constantly and traditional products such as saccharin, coumarin and acetates have been replaced by more complex organic compounds, with longer chains and increased value.

Searching the *National Institute of Industrial Property* and *Web of Knowledge* patent databases, throughout the period from 1980 to 2012, few registers were found which presented detailed descriptions of additives. Among the few reported additives are sodium citrate and sulfonic acid [1,2],which improve the brightness and corrosion resistance. Baths with sodium benzoate, saccharin,

uric acid, sodium sulfonate [3, 4] and thiazole [5–9] were also object of patents, and the last two were found to promote increase in corrosion resistance by the incorporation of sulfur in the nickel layer. In another register benzaldehyde and sodium disulfonate [10, 11] were used and, according to the authors, they provided better tensile strength to the deposited layers. Because the commercial formulations are proprietary, electroplating companies are required to follow strictly the dosage recommended by the suppliers. On the other hand, academic works are restricted to the baths prepared in laboratories, with a known and simpler composition, without reproducing exactly the commercial baths.

One of the most important characteristics of the electroplating bath is the throwing power, *i.e.*, its capacity of producing films with uniform thickness even when the distance of the cathode to the anode is not uniform along the piece to be plated, because of its irregular geometry. Since the throwing power is related to the Wagner number, any additive that increases (decreases) the cathode polarization or the electrolyte conductivity contributes to the increase (decrease) in the bath throwing power [12, 13].

The throwing power is the result of complex interactions between the different components of the bath and operating conditions. For example, Mohanty *et al.* [14] found that thiourea depolarizes the nickel reduction over the stainless steel substrate up to a concentration of 10 mg dm-3, but a mixed behavior was observed at higher concentrations.

In the decorative electroplating, the baths combine several additives to produce bright deposits on a wide range of current densities. The additives are commonly referred to as carriers, brighteners, and wetting agents, according to their main function. The carriers - also termed first class brighteners, secondary brighteners or control agents - interfere on the nucleation and growth of the newly formed phase, refining the deposit grain size and, consequently, producing brighter coatings with less internal stress. However, for the deposition of specular coatings, the use of brighteners - also termed second class brighteners, primary brightener or levelers – is required. The brighteners main role is to increase the bath leveling capacity, *i.e.*, its ability to deposit preferentially on defects and scratches on the surface, resulting in increasingly smooth surface, as the deposit increases in thickness. The wetting agents are tensioactive, facilitating the detachment of the gas bubbles generated by the hydrogen evolution reaction.

However, the mechanism of action of additives is complex and the influence of each additive on the properties of deposits is wider than one might suppose by the terminology described above. It is not uncommon that some specific property of a coating may result from the synergistic interaction between two or more additives in a bath of complex composition. For example, Ciszewski *et al.* [15] reported the synergistic effect of combination between saccharin and quaternary ammonium salts. Morkute and Bernotiene [16] demonstrated the interaction among saccharin, 2-butyne-1,4-diol and phthalimide. Mirkova and co-workers [17] demonstrated that the interaction among the operating conditions and the additives affects the degree of hydrogenation of the deposits, while the synergistic effect of applying pulsed current in combination with the use of the additives cis-2-butene-1,4-diol[18] and 2-butyne-1,4-diol [19] was demonstrated by Pavlatou *et al.*

These examples clearly show the importance of considering the interplay of additives. However, there is a predominance of studies addressing a single additive [20–25] and a surprising lack

of studies using factorial design of experiments, a technique specially suitable to reveal the interaction between experimental factors [26–30].

It is also noteworthy that most compounds identified in bibliographic studies are practically in disuse, as saccharin and coumarin. These additives are less efficient when compared to more advanced products and are still used only in small installations for cost-savings reasons. In the present study, last generation commercial additives were studied as an attempt to fill the gap between the scientific knowledge and the current practice of the nickel electroplating industry. The study consisted of the determination of the effects of additives on the properties of electrodeposits by means of a factorial design of experiments and Principal Component Analysis (PCA). The main purpose of the research was to find statistically relevant interactions between the additives for the determination of the coating properties.

2. EXPERIMENTAL

In the present study, three different kinds of commercial additives were used, consisting of one carrier, one brightener and one wetting agent. Active principles of each additive, according to the technical bulletin of the products provided by the suppliers, are listed on Table 1. As can be noted, the active principles of the additives consist of well-known surfactants. Both carrier and brightener have sulfonic compounds in their formulation.

Table 1. Commercial organic additives used and their active principles

Additive	*Active Principle*
Carrier	Sodium methanesulfonate
	Octane-1-sulfonic acid sodium salt
Brightener	1,4-butyne diol
	Ethylene sulfonic acid
Wetting agent	Alkyl or lauryl ether sulfate sodium salt

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Specimens of AISI 1020 carbon steel, 50 mm wide x 50 mm long x 0.3 mm thick, were plated in a Hull cell filled with a Watt's bath. Sample preparation was performed under similar conditions as those used in industrial processes, the salts concentration and the operational conditions are listed in Table 2, and the applied current density was 2 A dm^{-2}.Using the Hull cell geometry, it was possible to calculate the punctual average current density along the sample surface from the highest current density region [31]. All the reagents were of analytical grade and used without further purification.

In order to know the complete list of variables that significantly affect the electroplating a factorial design of experiments was used. Considering the large number of variables, a 2^{5-1} fractional factorial experimental was selected to reduce the number of experiments.

Table 2. Experimental parameters used in the electrodeposition.

Parameters	*Value*
pH	4.2
Temperature	55°C
Concentration of nickel sulfate	1.94 mol L^{-1} (300 g L^{-1})
Concentration of nickel chloride	0.62 mol L^{-1} (80 g L^{-1})
Concentration of boric acid	0.73 mol L^{-1} (45 g L^{-1})

The factors under study were: current density (i), charge (Q) and the dosage of each additive - brightener (B), carrier (C) and wetting agent (W). Table 3 presents the chosen levels for each studied factor.

Table 3. Factors and levels used in the factorial design (2^{5-1}).

Factor	Levels		
	+	C.P.	-
Current density (*i*)	6.06 A dm^{-2}	3.54 A dm^{-2}	1.03 A dm^{-2}
Deposition Charge (*Q*)	High	Medium	Low
Wetting Agent dosage (*W*)	3.0 mL L^{-1}	1.5 mL L^{-1}	0.0
Carrier dosage (*C*)	30 mL L^{-1}	15 mL L^{-1}	0.0
Brightener dosage (*B*)	1.0 mL L^{-1}	0.5 mL L^{-1}	0.0

The current density was calculated as a function of the cathode position through the equation expressed in Norm DIN 50957, which considers a primary current distribution in a Hull Cell filled with a standard Watt's bath. According to this equation, the levels indicated in Table 3 correspond to the average values of the current density between 2.0 and 3.0 cm (+) and between 7.0 and 8.0 cm (-) from the cathode end closest to the anode. After deposition, all specimens were divided into small samples of 1.0 cm and those corresponding to the desired current level were selected.

The deposition time was controlled in order to obtain the desired amount of charge. The inferior level for additives dosage chosen was zero, *i.e.*, absence of the additive and the superior level was chosen for being the recommended concentration for the industrial process.

Two center points (C.P.1 and C.P.2) were added. The trials were performed randomly. The matrix of the experiments is presented on Table 4, already contemplating the results.

Samples were characterized according to their brightness (Br), charge transfer resistance (Rct) and roughness (Rg). The measures for brightness were obtained by reflectance in a MICRO-GLOS 60° unit, BYK Gardner®, according to the ASTM D-523 – 89 standard, revised in 1999, denominated *Standart Test Method for Specular Gloss*. Charge transfer resistance was measured through electrochemical impedance spectroscopy, in an AUTOLAB® potentiostat, model μ3AUT71263, with a frequency response analyzer module. A conventional single-compartment glass cell, having the sample to be analyzed as the working electrode and a 0.5 M sodium chloride solution as electrolyte,

was used. A platinum foil as counter electrode and an Ag/AgCl reference electrode were employed. Equivalent circuit fitting was made with software NOVA 1.9 using a simple Randles circuit. Roughness was determined by a SHIMADZU® Atomic Force Microscope, model SPM 9600.

Table 4. Matrix of the experiments in the fractional factorial design including results for the three response variables measured.

| | Factors | | | | | Response variables | | |
Trial	i	Q	B	C	W	Brightness/B. U.*	Rg** / nm	R_{ct}*** / kΩ
1	-	-	-	-	+	3.20	182.80	185.84
2	+	-	-	-	-	12.90	130.59	2.37
3	-	+	-	-	-	1.40	264.19	5.74
4	+	+	-	-	+	5.30	150.54	78.01
5	-	-	+	-	-	80.80	53.59	218.84
6	+	-	+	-	+	71.60	32.32	198.19
7	-	+	+	-	+	66.10	66.07	124.70
8	+	+	+	-	-	97.10	137.74	136.86
C. P.1	0	0	0	0	0	153.30	33.84	134.88
C. P.2	0	0	0	0	0	143.40	43.85	142.67
9	-	-	-	+	-	66.70	56.95	22.66
10	+	-	-	+	+	104.40	31.68	228.85
11	-	+	-	+	+	60.40	43.72	258.81
12	+	+	-	+	-	126.50	33.28	68.04
13	-	-	+	+	+	126.00	13.17	86.84
14	+	-	+	+	-	59.10	22.98	34.12
15	-	+	+	+	-	7.60	157.45	27.06
16	+	+	+	+	+	409.10	3.42	147.49

* B. U – Brightness Units; **Rg – Roughness; ***R_{ct} - Charge transfer resistance

The main statistical tool used was principal component analysis. PCA enables the data set evaluation by decreasing the dimension of the data and conserving the most useful statistical information present in the original data. The statistical operations were performed using the software MINITAB 16.2.2.

3. RESULTS AND DISCUSSION

The results of the experimental factorial design are presented on Table 4, for the three response variables measured, namely, roughness, charge transfer resistance and brightness. Before proceeding with the statistical analysis, interesting results that can be observed in some individual trials were presented. Trial 2, which was accomplished without the presence of additives, presented the lowest charge transfer resistance, corroborating the assertion that the addition of organic additives increases corrosion resistance. Trial 1-4 yielded low brightness and high roughness, confirming the obvious

relation between these two variables. Since these trials were performed in the absence of carrier and brightener, the importance of these additives to obtain bright deposits was demonstrated, as presented by Pavlatou *et al.* [19]. However, in view of trial 15 which also resulted in high surface roughness and low brightness, despite the use of both brightener and carrier, the influence of the wetting agent on the quality of the deposit should be considered, a fact often denied in the industry. It is also noteworthy that trial 16, prepared in the presence of all three additives, produced the deposit with the highest brightness, lowest roughness and a relatively high charge transfer resistance. Trial16 brightness value was over six times higher than the standard deviations for the average brightness of the other trials, indicating a non-linear behavior of this variable. It is important to note that such abrupt variation was not observed for the other variables measured in the same sample, but to eliminate any possibility of experimental error, this trial was repeated and the brightness value was confirmed.

Brightness variation can be better understood when its correlation with the roughness of the deposit shown in Figure 1 is considered.
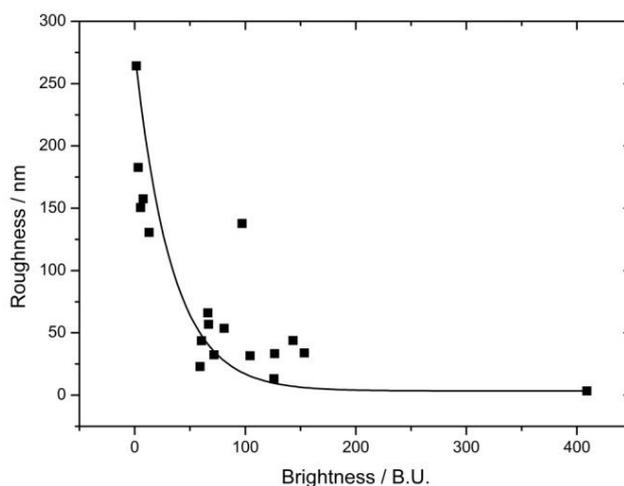
Figure 1. Correlation between roughness and brightness values. The line is only a guide for the eye.

Roughness decrease is directly correlated to the increase in brightness, up to values of 100 nm average roughness. Below this value, the depressions have depths in the order of, or less than, the wavelength of light and thus, further roughness decrease does not imply increased brightness. In this situation, the brightness seems to be determined by other factors such as crystal size and texture of the deposit which in turn are determined by the interplay among the three additives and process parameters, a similar result was observed with the usage of different additives by Bernotiene *et al.* [16]. In view of the fact that the brightness is controlled by different causes below and above a threshold value for the average roughness, it seems reasonable to assume a non-linear variation in relation to the factors under study.

The values calculated for the factor effects were listed in Table 5, each column for a variable response. Entries labeled with asterisks indicate that the respective factors were not included in the model, given the statistical significance, as indicated by ANOVA. In the first column of Table 5 we

can verify that the effects calculated for brightness are all positive but one. This result must be viewed with caution since the model presents a lack of fit, probably due to the outlier. One option to eliminate the influence of the outlier is discard it and analyze the design with trial 16 treated as a missing value [26]. Despite the non-orthogonality of the resultant design, the effects can be calculated by least-square methods [26] and the values were listed in the second column of the table. Another option, when the ratio between the maximum and minimum response value is large, is to apply a power transform on the original data ($y* = y^\lambda$).[26] The third column in Table 5 presents the effects calculated for the transformed response, obtained by the square root of the original data ($\lambda=0.5$, determined by Box-Cox method). In this case, the effect absolute values are not comparable with the previous two, and the relative contributions should be used instead.

Comparing the second and third columns of Table 5 it is apparent that the different analyzes on the brightness response produced essentially the same results, i.e. the most influential factors are B, C, i, i*Q, B*W, C*W and B*C. Figure 2 shows interaction plots for the four above-mentioned terms. Increasing current density increases the brightness due to grain size reduction, but this effect is much more pronounced at the high level of charge, as shown in Figure 2a. Figures 2b and 2c show that the wetting agent interacts synergistically with the brightener and carrier, respectively [15]. Figure 2d shows that the brightener effect is reduced in the presence of a carrier.

Table 5. Calculated effects and their relative influence on the three response variables.

Terms	Brightness (including trial 16)	Brightness (excluding trial 16)	(Brightness)$^{0.5}$	Roughness	Charge transfer resistance
Main Effects (% Contribution)					
Current (i)	59.23 (9.34)	29.73 (5.23)	2.95 (9.17)	-36.92 (6.20)	-4.57 (0.07)*
Charge (Q)	31.10 (2.58)	1.60 (0.01)*	0.42 (0.18)*	41.54 (7.85)	-16.38 (0.97)*
Brightener (B)	67.08 (11.98)	37.58 (8.35)	3.88 (15.92)	-50.88 (11.78)	15.47 (0.86)*
Carrier (C)	77.68 (16.07)	48.18 (13.73)	4.37 (20.21)	-81.90 (30.53)	-9.59 (0.33)*
Wetting Agent (W)	49.25 (6.48)	19.75 (2.31)	2.08 (4.57)	-41.63 (7.89)	99.13 (35.46)
2nd order interactions (% Contribution)					
i*Q	66.40 (11.74)	36.90 (8.05)	3.00 (9.50)	-14.69* (0.98)	8.09 (0.24)*
i*B	29.88 (2.38)*	0.38 (<0.01)*	0.84 (0.74)*	13.47* (0.83)	19.38 (1.35)*
i*C	50.38 (6.76)	20.88 (2.58)	1.92 (3.88)	-8.06 (0.30)*	25.35 (2.32)*
i*E	24.45 (1.59)*	-5.05 (0.15)*	0.13 (0.02)*	14.97* (1.02)	3.66 (0.05)*
Q*B	29.50 (2.32)*	~	0.73 (0.57)*	19.11* (1.66)	-9.09 (0.3)*
Q*C	30.75 (2.52)	1.25 (<0.01)*	0.76 (0.61)*	-13.27* (0.80)	48.61 (8.52)
Q*W	27.83 (2.06)*	-1.67 (0.02)*	1.27 (1.69)*	-40.60 (7.50)	-6.30 (0.14)*
B*C	-6.12 (0.1)*	-35.63 (7.51)	-2.76 (8.04)	58.72 (15.69)	-86.19 (26.80)
B*W	57.80 (8.9)	28.30 (4.75)	2.61 (7.18)	-22.56 (2.32)	-64.05 (14.80)
C*W	60.75 (9.83)	31.25 (5.78)	2.81 (8.37)	-3.04 (0.04)*	43.40 (6.80)

The fourth column in table 5 lists the effects calculated for roughness, showing that the carrier is by far the main factor that accounts for over 30% of the total variance. The greatest interaction effects are B*C, Q*W and B*W being that B*C and B*W have the opposite effects for brightness. It is interesting to note that the main factor Q and its interactions with W do not present significant effects for brightness.
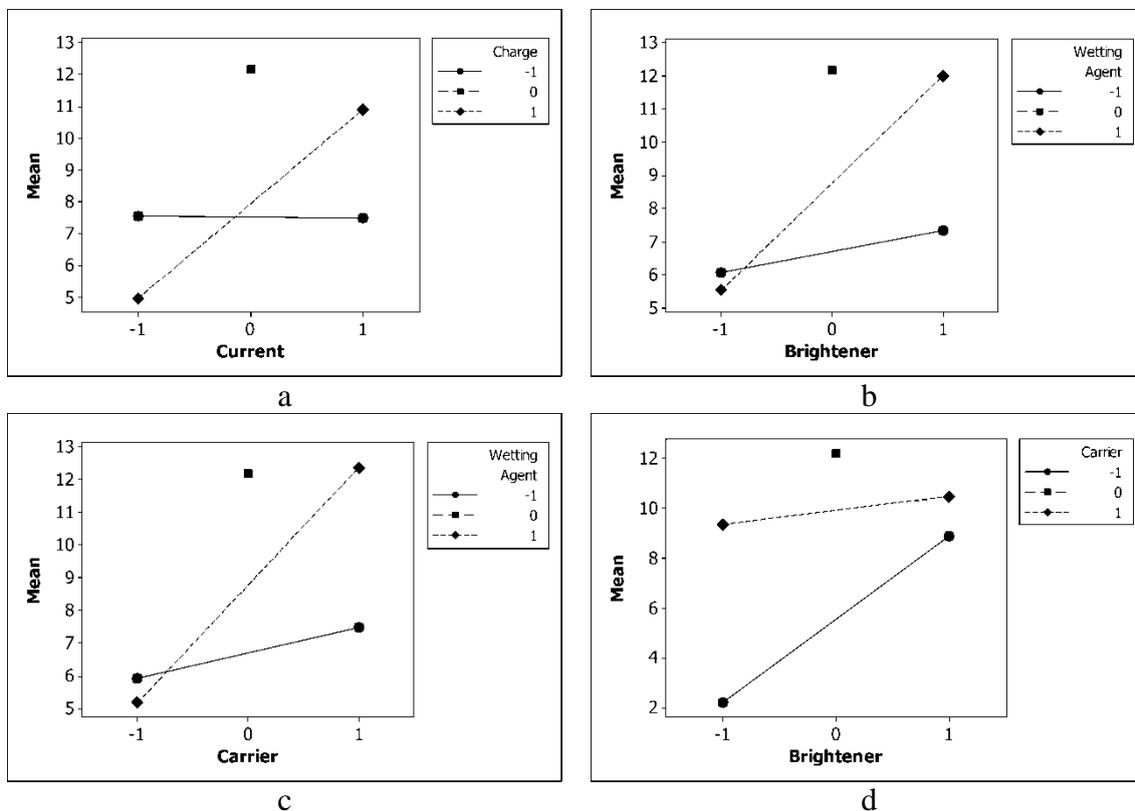
Figure 2. Interaction plots for (brightness)$^{1/2}$: current and charge (a); brightener and wetting agent (b); carrier and wetting agent (c); carrier and brightener (d).

Figure 3 shows interaction plots for roughness. The antagonistic interaction between brightener and carrier and the synergistic interaction between brightener and wetting agent are shown in Figures 3a and 3b, respectively [16]. Figure 3c shows that in the absence of a wetting agent, the factor carrier contributes significantly to increase roughness while in the presence of a wetting agent this effect is suppressed. This fact, together with the results shown in Figures 2b, 2c and 3b demonstrates the importance of a wetting agent to reduce surface roughness and improve brightness, which is not recognized in the industrial practice. Another important and somewhat unexpected result is the antagonistic effect between brightener and carrier, suggesting a mutual compensation on the electrode polarization by these two additives.
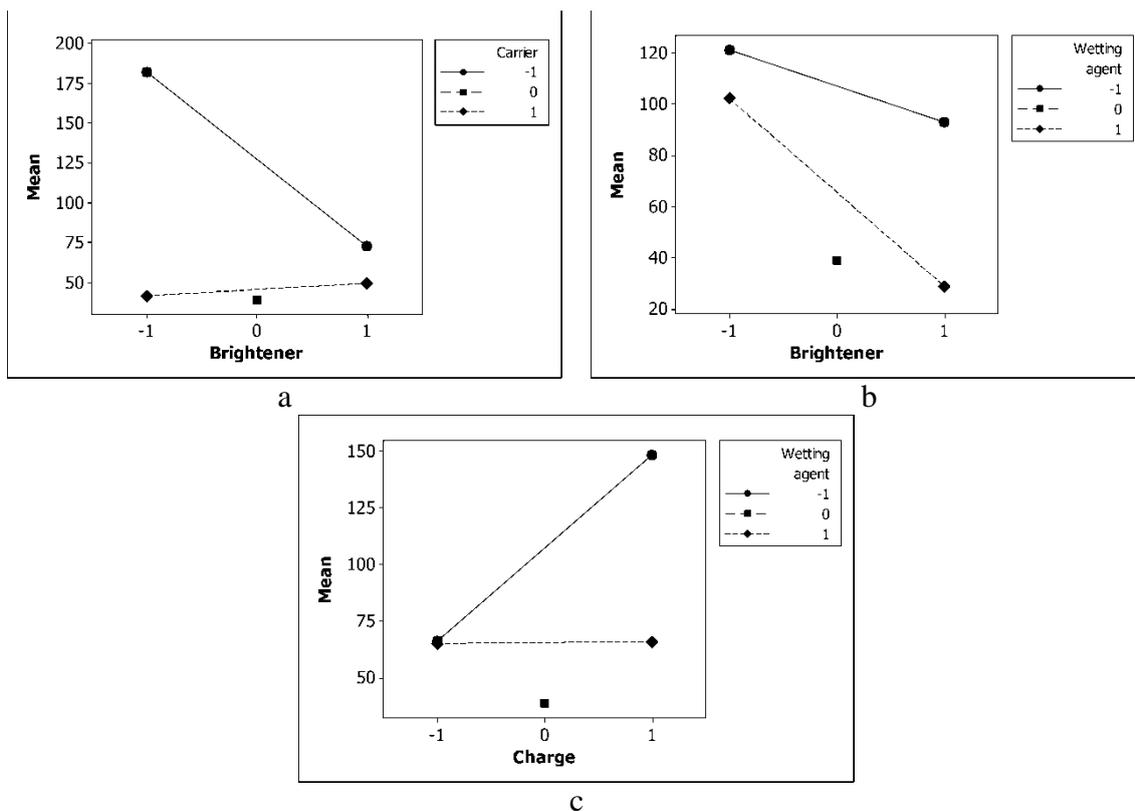
Figure 3. Interaction plots for roughness: brightener and carrier (a); brightener and wetting agent (b); charge and wetting agent (c).

The last column in Table 5 lists the effects calculated for charge transfer resistance. Again, we found a high prevalence of one of the factors, the wetting agent in this case. This can be understood by considering that in the absence of a wetting agent, hydrogen bubbles led to the formation of holes in the deposit resulting in a low charge transfer resistance.

Figure 4 shows interaction plots for charge transfer resistance including the four second order terms that have the highest effects.
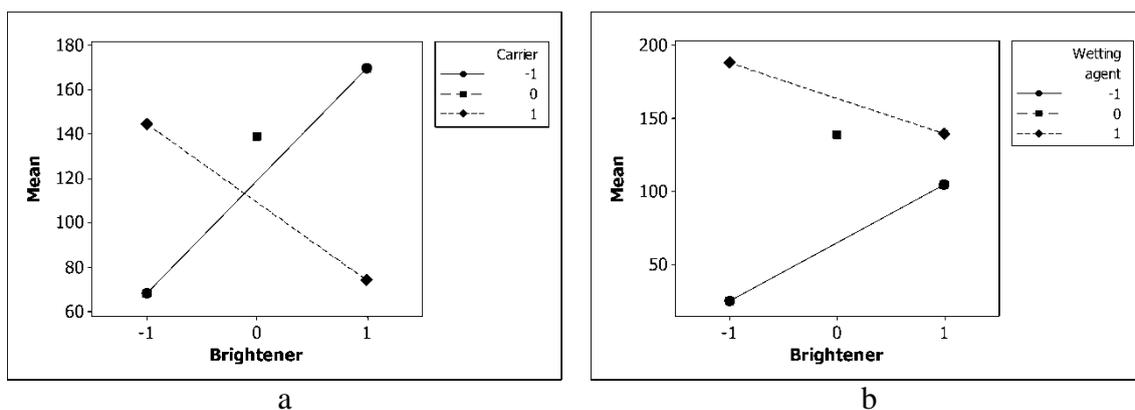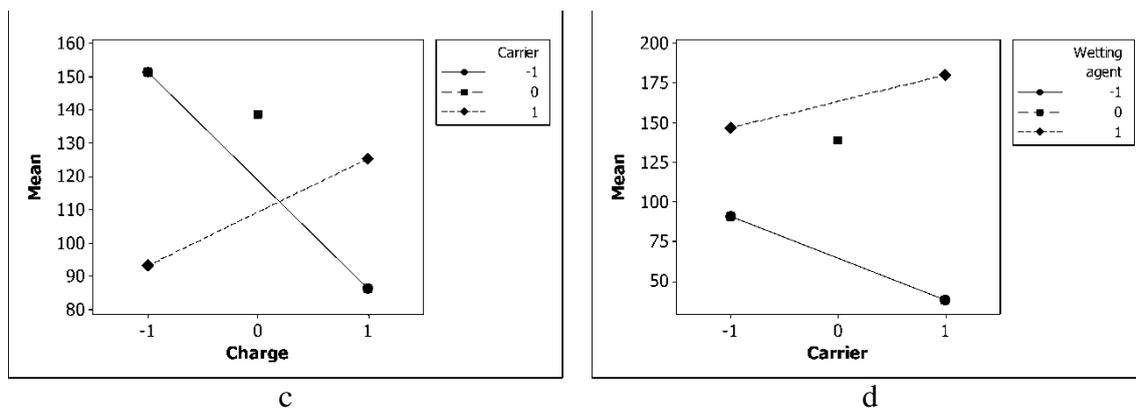
Figure 4. Interaction plots for charge transfer resistance: brightener and carrier (a); brightener and wetting agent (b); charge and carrier (c); charge and wetting agent (d).

It is interesting to note that although the main effects of factors charge and carrier are negligible their second order interaction is very important. It is also noteworthy that the term B*W has an antagonistic interaction for charge transfer resistance and a synergistic interaction for the other two response variables.

The results above show the importance of experimental design in the evaluation of the additive effects [29]. Since the interactions between additives are easily captured, the results serve as an excellent guide for further investigations in order to disclose the additive mechanisms of action. Also, by means of a response surface and additional optimizations, it is possible to find the best formulation for a bath that it will not necessarily be identical to that indicated by the vendors.

Analyses of the results obtained revealed the great importance of the studies performed concerning the industrial application since they allow us to assess the interaction effects between the additives. These analyses also demonstrate the possibility of changes on the electrodic solution which permits electrodeposition efficiency improvement, enhancement of the nickel plate properties and reduction in the costs of the deposition process. The former three factors are not usually considered in the productive media. Recent literature survey does not show any research focused on this sort of evaluation, moreover concerning these 3 types of additives, frequently used in commercial nickel electrodeposition baths.

Principal component analysis was applied to the experimental data to check for possible similarities and/or differences between experiments as well as correlation between the variables. After the development of the PCA, the first and second principal components captured 60.51 % and 26.25 % of the variance of the experimental data, respectively, together totaling 86.76 % of variance captured. Figure 5 (b), shows through factor 1, that the roughness was negatively correlated to the brightness. Considering the distribution of the experiments in Figure 5 (a), trials 5, 6, 10, 11, CP1, CP2, 12, 13 and 16 appear in the positive axis, indicating their better performance in relation to charge transfer resistance and brightness. Moreover, among these experiments, only in trial 5 the brightener was used without combination with another additive, which suggests that the brightness is not provided solely by the addition of this additive.

On the other hand, trials 1, 2, 3, 4 and 15 appear in the negative axis, showing their high roughness, low brightness and low charge transfer resistance. Trials 9, 14, 7 and 8, in turn, appear in the center of the axis, indicating that they are intermediate results in relation to Factor 1.

Figure 5 (b) also shows that roughness is less explained by Factor 2 (26.25 %), since it is located near the center of the axis, while brightness appears inversely proportional to the charge transfer resistance. This last fact has technological relevance, since it shows that not all factors that lead to increase in brightness lead to increased corrosion resistance. Thus, the PCA proved to be very important for the assessment of the quality of the deposition bath.
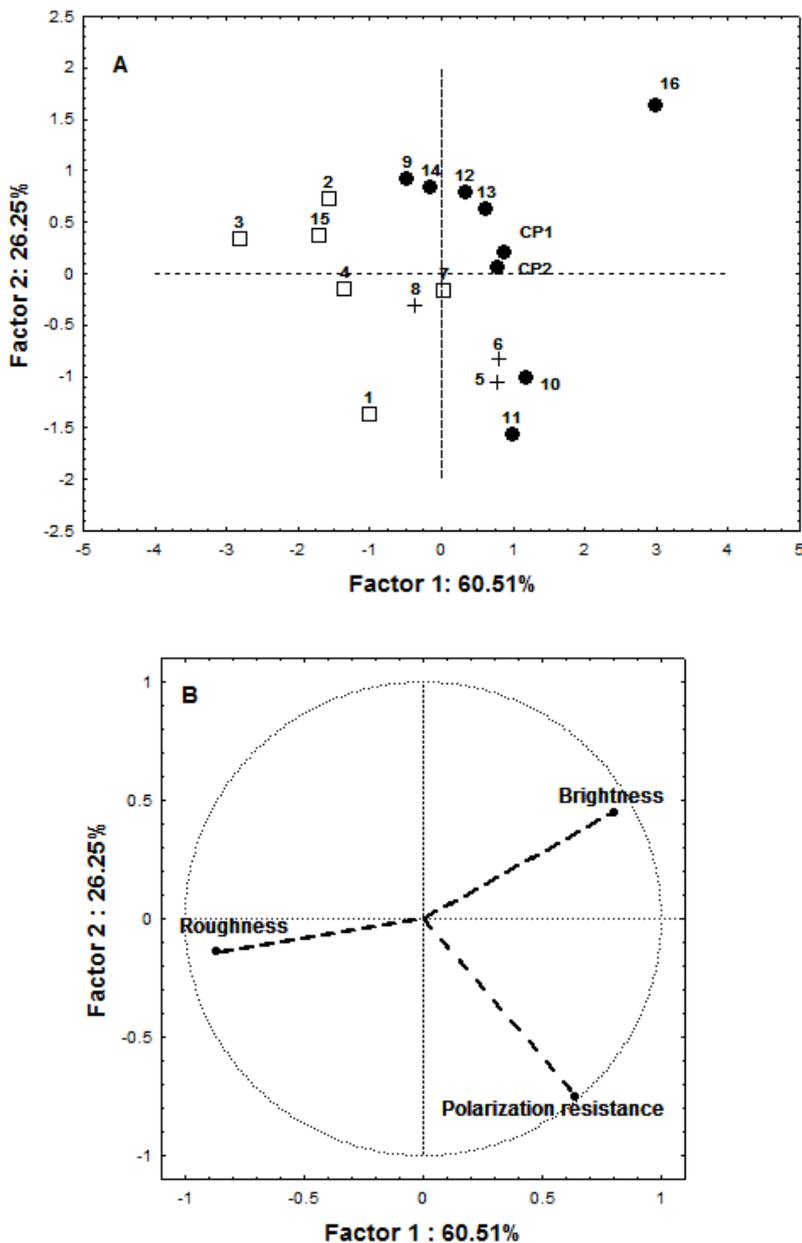
Figure 5. (a) Scores of factorial design (symbols □, + and ✱ indicate similar morphology groups) and (b) loadings of variables (brightness, roughness and charge transfer resistance) on the plane defined by the principal components of PCA analysis.

Regarding morphology, samples can be divided into three characteristic groups which almost correspond to the samples distribution in the plane of PCA. The symbols used in the Figure 5 (a) indicate the samples belonging to each group with similar morphology characteristics.

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Figure 6 shows images of atomic force microscopy representing typical morphological features for each group. In the first group (trials 1-4, 7 and 15), the planar faces of the nickel crystal structure are clearly distinguished, showing a random face orientation which suggests a tridimensional growth. This group presented high surface roughness ranging from 60-270 nm and, except for trials 7 and 15, consisting of samples plated without carrier and brightener.
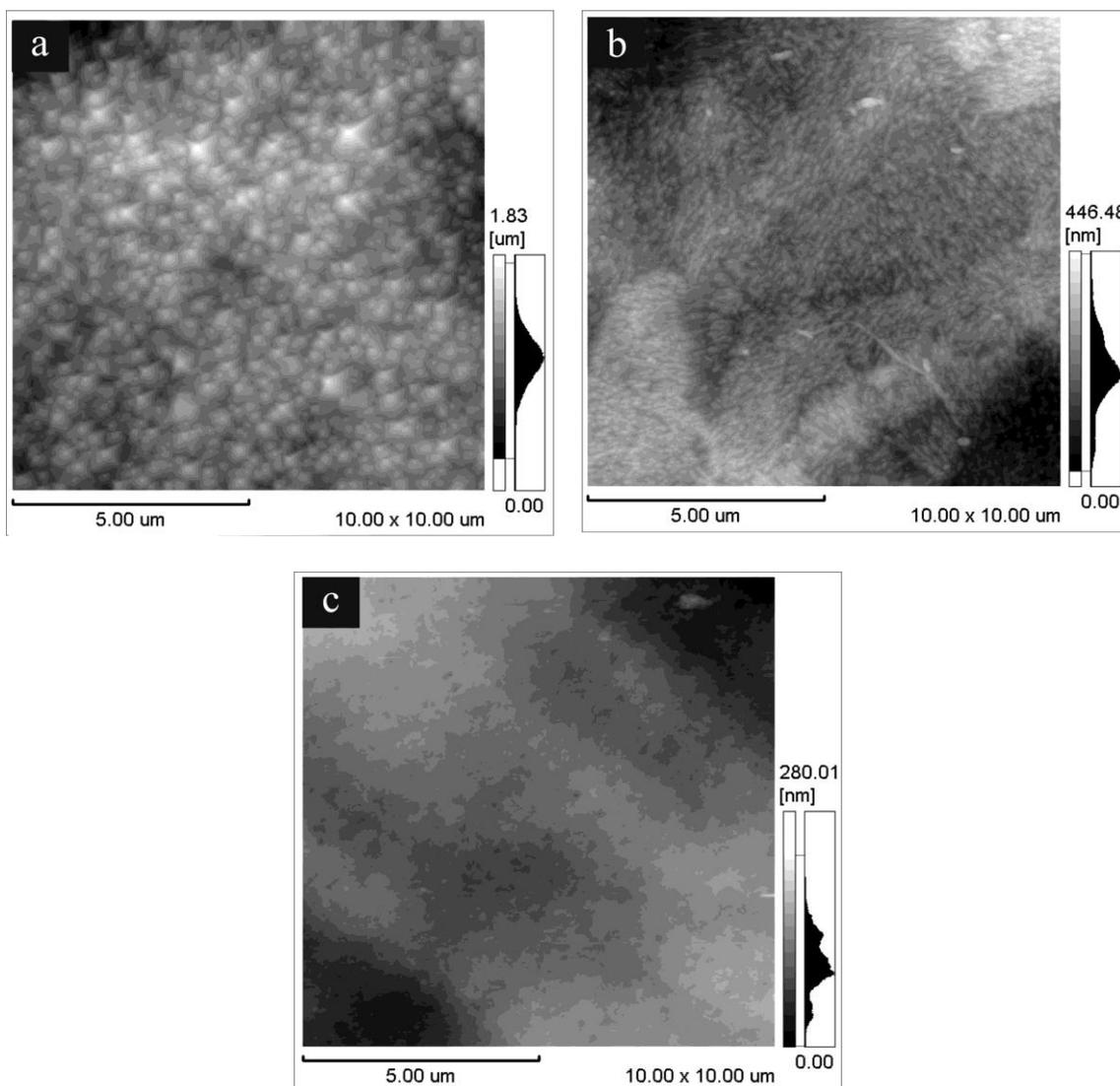
Figure 6. Typical morphologies for a deposit formed a) Group 01: without brightener and carrier b) Group 02: with brightener and without carrier c) Group 03: without brightener and with carrier.

In trial 7, the size of the crystal was considerably smaller than the other samples of the group, which explains its higher brightness. Trial 15, in turn, presented a somewhat different morphology, showing a columnar growth of the deposit (not shown).

In the second group (trials 5, 6 and 8) needle-like crystals appeared. This group presented intermediate roughness, ranging from 50 to 140 nm. The experimental condition common to these trials is the absence of carrier in the deposition bath.

The third group (trials 9-14 and 16) presented smoother coatings in which the crystal faces are not distinguished, suggesting a two-dimensional growth. In this group, all the samples were plated with the addition of carrier, being that the samples that fell in the first quadrant of the PCA plane were plated with the addition of brightener and carrier. The samples belonging to this group presented roughness between 3.0 and 60 nm, the lowest roughness among all the trials, this observation corroborate whit the finds that the addition of brightener promote a decrease on the superficial roughness, as showed by Pavlatou *et al.* [19] and Oliveira *et al.* [25].

It is interesting to compare the morphological groups as defined above with the distribution of the trials in the plane defined by the principal components of PCA. It is noted that the trials with similar morphology are grouped together in the PCA plane as indicated by the symbols in Figure 6 (a). A notable exception to this rule arises from trials 5, 6, 10 and 11, which appear grouped together in the fourth quadrant, despite their different morphologies. This observation leads to the conclusion that the charge transfer resistance, unlike brightness and roughness, is not fully determined by the coating morphology, and this is another aspect pointed out by this investigation.

4. CONCLUSIONS

In the present study, we demonstrated the benefit of using factorial design to study nickel electroplating baths. Several synergistic and antagonistic effects were revealed and briefly discussed on a physical basis. PCA proved to be a very important tool to discriminate the effects of the additives. The first and second principal components captured 60.51% and 26.25% total variance of the experimental data, respectively. Roughness was negatively correlated to the brightness through factor 1 while polarization resistance was negatively correlated with brightness through factor 2. Clustering in PC-space can be associated with morphological characteristics of the coatings. The novelty of this paper is related to the possibility of evaluating the interactions between the three additives under study, which are frequently used in the industrial preparation of nickel plates. This evaluation opens the possibility of changes in the deposition condition for the production of better films, which result in better energy efficiency and cost reduction. Besides those findings, the analysis of the results allowed us to show that the wetting agents does affect the film properties and the efficiency of the deposition process. Those observations are important to understand the electrodeposition mechanism and then make possible a proposition of new addictive formulations to commercial Nickel electroplating. We believe that this is the novelty offered by our paper.

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