# N-Heterocyclic Organic Compounds as Additives In the A-C Coloring of Anodized Aluminum From Nickel Sulfate Solutions Part I: Effect on Color Intensity and Uniformity of the Probes

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The 2-, 3-, and 4-piperidinecarboxylic acids, the 2-, 3-, and 4- pyridinecarboxylic acids, as well as L-proline, Lhydroxyproline and L-azetidine-2-carboxylic acid were used as additives in the electrolytic coloring of anodized aluminum from nickel(II) sulfate-boric acid solutions. Their influence on the color uniformity (TP) and color intensity of the probes was investigated and correlated with their structure. This influence seems to depend on their aromatic or saturated character, the position of the carboxyl group in the molecule and, finally, on the number of carbon atoms in their rings.

During the two-stage electrolytic process,<sup>1,2</sup> aluminum is first anodized in sulfuric acid solution, followed by electrolytic deposition of a metal (tin, nickel or cobalt) at the base of the pores of the anodic coating by means of an alternating current.

The nickel electrolytes,<sup>3</sup> in comparison with the tin(II) sulfate electrolyte, are relatively inexpensive, but they are sensitive to contamination by ions, have a tendency to form complex compounds and have poor throwing power (TP),<sup>4,5</sup> and, consequently, poor color uniformity. There are not many organic additives known that are suitable, however, for the improvement of TP of the nickel sulfate solutions.<sup>69</sup> This can be explained by the complexing properties of nickel(II) ions.<sup>10,11</sup>

In a previous study,<sup>12</sup> several N-heterocyclic compounds were used as additives to improve the TP of tin(II) solutions. It was recognized that the piperidine-4-carboxylic acid has a positive influence on TP of tin sulfate solutions. This fact was further confirmed in the case of nickel(II) solutions.<sup>13</sup>

In this study, the influence of a series of N-heterocyclic saturated and aromatic organic compounds (Fig. 1) on the TP of nickel sulfate solutions was investigated. An attempt has been made to correlate the saturated or unsaturated nature of these compounds, the number of carbon atoms in their rings, and the position of the -COOH group in the nucleus, with their effect on TP of the baths and the color intensity of the probes. Among the above compounds, there are two amino acids, proline and hydroxyproline, the use of which has been referenced,<sup>7</sup> for the electrolytic coloring of anodized aluminum from nickel sulfate solutions in high concentrations and without the use of boric acid.

## Experimental Procedure

Test specimens of 1050 aluminum alloy foil with dimensions  $2 \times 4 \times 0.1$  cm were used. The surface of the specimen, except for a unit area 10.7 cm<sup>2</sup>, was covered with araldite (epoxy resin). All the samples were degreased in acetone, etched for 1 min in a solution containing 100 g/L sodium hydroxide at 60 °C, rinsed well and immersed for 1 min in 1:1 v/v nitric acid at room temperature. They were rinsed in tap water, then rinsed in deionized water.

The anodizing was carried out in 15-percent w/v sulfuric acid solution at  $20 \pm 2$  °C (with cooling and agitation) for 25 min at a constant potential of 18 V. After anodizing, the samples were rinsed in tap water and subsequently in deionized water for 1 min. The electrolytic coloring then took place at 15 VAC in a 100-mL bath containing 30 g/L of nickel sulfate (NiSO<sub>4</sub> · 6H<sub>2</sub>O) and 30 g/L boric acid (reference solution, T) and the additives as referred in Tables 1-3, for 10 min at  $20 \pm 1$  °C. A variable transformer<sup>a</sup> was used to control the applied voltage. The counter-electrode was stainless steel.

The thickness of the oxide layer was measured<sup>b</sup> and found to be  $15\pm2\,\mu\text{m}$ . The specific conductivity was measured with a conductivity meter<sup>c</sup> at 25 °C.

The aluminum specimens used for the determination of throwing power had dimensions of 20 x 10 cm and were electrolytically colored in a specific cell<sup>13</sup> at  $20 \pm 1$  °C for 10 min at 15 VAC. The throwing power was expressed as a percentage of the length, which was uniformly colored over the total length of the specimen. A range of values of TP occurs because of a gradual lowering of the color intensity of the surface. The spectral reflectance of the specimen surface was measured by spectrophotometer<sup>d</sup>.

<sup>b</sup> Permascope, Fischer Technology, Inc., Norwalk, CT

<sup>c</sup> Model CMD 83, Radiometer Copenhagen (Denmark)

d CM-2002 Minolta



Fig. 1—Molecular structure of N-heterocyclic additives. The upper three compounds have a saturated six-membered ring; the middle three have an unsaturated six-membered ring; the lower three have saturated five- and four-membered rings.

<sup>&</sup>lt;sup>a</sup> NCSR DIMOKRITOS (0-50 V, 1-5 A)

#### Table 1

Influence of the Concentration of Additives (B)	and
(C) on pH and Throwing Power (TP).*	

Solution	Conc. (g/L)	pН	% TP
B1	0.04	3.50	15-30
B2	0.07	3.50	40-80
B3	0.15	3.40	40-70
B4	0.30	3.30	40-70
C1	0.03	3.40	20-50
C2	0.05	3.26	25-50
C3	0.07	3.25	30-80
* For referen	and colution T: nH 2	50 and TD $-2$	0.40 percent

\* For reference solution T: pH 3.50 and TP = 20-40 percent. (B) Piperidine-3-carboxylic acid; (C) Piperidine-2-carboxylic acid

Table 2 Influence of the Concentration of Additives (D), (E) and (F) on pH and Throwing Power (TP)

Solution	Conc. (g/L)	pH	% TP
D1	0.03	3.30	20
D2	0.07	3.00	25
D3	0.14	2.90	*
E1	0.03	3.40	25
E2	0.09	3.25	20
E3	0.14	3.00	50
E4	0.28	2.90	*
F1	0.04	3.00	25
F2	0.09	2.70	*
F3	0.14	2.60	*

\* Significant inhibition of coloring.

(D) Pyridine-4-carboxylic acid; (E) Pyridine-3-carboxylic acid;

(F) Pyridine-2-carboxylic acid

## Table 3

Influence of the Concentration of Additives (G), (H) and (I) on pH and Throwing Power (TP)

anu		ITOWING POWEL	(IP)
Solution	Conc. (g/L)	pН	% TP
G1	0.026	3.50	15-35
G2	0.065	3.25	25-50
G3	0.092	3.10	20-40
G4	0.130	3.00	15-35
H1	0.149	3.20	20-40
H2	0.298	2.90	40-70
H3	0.447	2.85	40-70
H4	1.490	2.85	40-80
H5	5.900	2.60	40-80
I1	0.014	3.50	25-50
I2	0.019	3.20	40-70
I3	0.023	3.10	25-50

(G) L-proline; (H) L-hydroxyproline; (I) L-azetidine-2-carboxylic acid

# Results and Discussion

From the pH values listed in Tables 1–3, it is obvious that the pH of the solutions is altered by the additives. The pH decreases slightly with increase of concentration of piperidine-3-carboxylic acid (B) and much more so with increase of concentration of piperidine-2-carboxylic acid (C) (Table 1). This latter additive is coordinated<sup>14</sup> with nickel(II) preferentially in the anionic form (NHC<sub>5</sub>H<sub>o</sub>COO-), although it is entering the solution as a neutral molecule, which is largely zwitterionic (+NH<sub>2</sub>C<sub>5</sub>H<sub>6</sub>COO-) and extremely unreactive.<sup>15</sup> Accordingly, for the nickel(II) complex to be formed,<sup>14</sup> a deprotonation of the amino acid grouping takes place and a lowering of pH of the above solutions is observed (Table 1). The ring closure seems to take place after elimination of the first water molecule from the inner co-ordination sphere of the nickel ions, which is the rate determining step.<sup>16</sup> The respective lowering of pH doesn't take place to this extent in the case of additive B, because the formation of the chelate ring is not thermodynamically favored.17

In the case of additive piperidine-4-carboxylic acid, (A), an enhancement instead of lowering of pH has been observed with increase of its concentration in the solution<sup>13</sup> in the range: 0.03 g/L (A1), 0.05 g/L (A2), 0.07 g/L (A3) and 0.14 g/L (A4). This probably means that the zwitterion, when entering the solution, is protonated, taking protons from the acidic bath  $(+NH_2C_5H_0COOH)$ . The possibility of formation of a chelate compound is not stereochemically favored. With increase of the concentration of the additives pyridine-4carboxylic acid (D), pyridine-3-carboxylic acid (E) and pyridine-2-carboxylic acid (F), the solutions become more acidic (Table 2). This release of protons derives from the deprotonation of the zwitterion (+NHC<sub>5</sub>H<sub>4</sub>COO-) to the anion (NC<sub>5</sub>H<sub>4</sub>COO-), which is the attacking form. This is more obvious in the case of the 2-isomer (additive F), the complex compounds of which with nickel(II) ions are very stable in the pH range of the respective solutions.<sup>18</sup>

The amino-acids proline (G), L-hydroxyproline (H), and L-azetidine-2-carboxylic acid (I) have been added to the solutions in the acid form, resulting in a lowering of pH of the above solutions (Table 3). The complexation of nickel(II) with these ligands is not favored in these acidic solutions.<sup>15</sup> Moreover, proline is among the most reactive ligands, while L-hydroxyproline is among the less reactive<sup>19</sup> because the coordinated water molecules of the metal ion may be hydrogen-bonded to the hydroxy-group of the ligand.

The specific conductivity of the solution T is 1.035 mS/cmand that of the other electrolytic coloring solutions is practically the same ( $\pm 0.01 \text{ mS/cm}$ ).

From Tables 1-3, it can be seen that the TP is improved by the presence of the additives at a certain range of concentrations, with the exception of D and F. It is also observed that in the case of aromatic additives, the color intensity of the probes becomes obviously worse.

The influence of the above additives on TP was determined more precisely by measurement of the spectral reflectance of the colored probes at sites of increased distance from the counter-electrode, at concentrations which showed the best results. According to the data of Tables 1-3, the more appropriate coloring baths were: A3, B2, C3, D2, E3, F1, G2, H4 and I2. The reference solution T was also used for comparison. The total reflectances were calculated from the respective spectral reflectances and were converted to absorbance values<sup>20</sup> which, in conjunction with the distance from the counter-electrode, are shown in Figs. 2-4. The results were



Fig. 2—Absorbance of the anodized aluminum probe (blank) and of the electrolytically colored probes in solutions *T*, *A3*, *B2* and *C3* as a function of the distance from the counter-electrode.

fitted by three-degree polynomials. If it is considered that the absorbance values, which are related to the amount of deposited nickel on the probe, decrease almost linearly until the first 7-9 cm, then the TP can be expressed by the absolute value of the fitted one-degree polynomials (Table 4). If this value tends to zero, the TP is improved. This means that the uniformity *of color* of the probes is also improved.

It should be noted from these data, as in the previous conclusion, that all additives, except D and F, improve the TP under a certain range of concentrations. Accordingly, it was observed that the piperidine-4- and piperidine-3-carboxylic acids and L-hydroxyproline have the best influence on TP. The 2-substituted saturated compounds improve also the TP in the order of increase of the carbon atoms of their rings. From N-heteroaromatic compounds, only the 3-isomer improves the TP, but all of them considerably diminish the color intensity.

The amount of deposited nickel on a total colored area of  $62.3 \text{ cm}^2$  after 10 min of coloring is a measure of the color intensity of the probes. This is expressed in the present study by the total absorbance, which was calculated by integration of the curves of Figs. 2, 3 and 4 (Fig. 5).

Fit by One-degree Poly 2, 3 and 4 for the D	Table 4 nomials of Results from Figs. First 7-9 cm of the Probe
Solutions T A3 B2 C3 D2 E3 F1 G2	Linear Y = AX + B Y = $-0.102X + 1.27$ Y = $-0.063X + 1.17$ Y = $-0.060X + 1.09$ Y = $-0.068X + 1.17$ Y = $-0.096X + 0.96$ Y = $-0.058X + 0.68$ Y = $-0.104X + 1.16$ Y = $-0.076X + 1.14$
H4 I2 Blank	$\begin{split} Y &= -0.062X + 1.14 \\ Y &= -0.077X + 1.18 \\ Y &= 0X + 0.19 \end{split}$



Fig. 3—Absorbance of the anodized aluminum probe (blank) and of the electrolytically colored probes in solutions T, D2, E3, and F1, as a function of the distance from the counter-electrode.

It is obvious from Fig. 5 that additive A has the best influence on color intensity, that the C and H additives also improve it, that the B, G and I don't alter it significantly, while the aromatic additives D, E, and F have a very negative influence.

The observed inhibition of nickel(II) deposition seems to be derived from the aromatic character of these additives, which permits them to produce stable compounds with nickel(II) ions, in the pH range of the respective solutions, on the electrode surface.

On the other hand, the positive action of saturated additives is significant for both color intensity and TP and it appears to depend mainly on the position of the carboxyl group and, to some extent, on the size of their ring and the permitted or favored stereochemistry.<sup>17</sup> They are readily adsorbed on the electrodes without using  $\pi$ -electrons, but using only n-electrons of the heteroatom and dipole-dipole interactions because of the polarizability of the molecule and the ability of the substrate to generate positive/negative sites close together.

Other interactions with the substrate are also possible; for example, some protonation of the weaker carboxylate of the additives by the stronger acid  $[Al(H_2O)_6]^{+3}$  for some hydrolysis to take place. The complex formation of the additive C with the  $[Al(H_2O)_6]^{+3}$  species and the appearance of the tridecameric cation,  $[Al_{13}O_{40}H_{48}]^{+7}$  are referenced elsewhere.<sup>21</sup>

#### Conclusions

The main factor that determines the behavior of the Nheterocyclic acids during A-C coloring of anodized aluminum from nickel sulfate-boric acid electrolytes is their aromatic or saturated character. It may be concluded that the aromatic character has a very negative influence on color intensity, probably because of the formation of stable compounds with nickel(II) ions and that only the pyridine-3carboxylic acid among the aromatic types improves the TP. This can be explained by the fact that the carboxyl group, being in the 3-position is not involved in the resonance of the molecule and does not inhibit the formation of a momentary



Fig. 4—Absorbance of the anodized aluminum probe (blank) and of the electrolytically colored probes in the solutions T, G2, H4 and I2, as a function of the distance from the counter-electrode.



Fig. 5-Integration of the curves of Figs. 2, 3 and 4.

dipole. The latter facilitates adsorption of the additive on the electrode surface.

The saturated additives have a positive influence on both the color intensity and color uniformity of the probes in the order: A > C, H > B > G, I.

The positive role of these additives may be explained on the basis of their specific molecular structure, which allows them to have their molecules in the right conformation. Accordingly, the piperidine-4-carboxylic acid, which can be considered as the best, seems to function as a dipole that is adsorbed on the electrode surface and permits improvement of both TP and color intensity. Probably, the adsorbed additive increases the amount of metal ions on the electrode and accelerates the rate of flow of electrons through them from the electrode to the metal ions (ion bridging).<sup>22</sup>

The relative position of the functional group in the molecule also plays an important role. Accordingly, the piperidine-3-carboxylic acid improves the TP probably by a blocking effect, but not the color intensity. We will examine these two additives further for their mode of action to elucidate it more precisely. In the case of the 2-substituted saturated additives, the mechanism of complex formation of nickel(II) with them seems to facilitate either partial desolvation of the aqua-complexes of the metal ions during the adsorption process, or substitution of the water with an ion bridge.<sup>22</sup>

The number of carbon atoms in the rings appear to exert an influence that will also be investigated further in the near future.

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