

## Effect of a Natural Brightener, Daphne gnidium L. on the Quality of Nickel Electroplating from Watts Bath

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**Abstract:** *Daphne gnidium L. (DGL), a plant known to be rich source of polyphenols, a naturally occurring class of antioxidants, was tested for its ability to play the role of primary and secondary brighteners for electrodeposition of nickel, as a replacement for synthetic brighteners such as glycerol and formaldehyde. A simple and convenient approach was adapted consisting in adding an accurate amount of powdered leaves of Daphne gnidium L. (DGLP) or Daphne gnidium L. leaves extract (DGLE), to the Watts bath, to play the role of brightening agents. Cyclic voltammetry studies revealed that DGLP could inhibit the reaction of nickel reduction and improve the quality of the deposits as efficiently as glycerol and formaldehyde. SEM analyses showed that the micro-cracks decreased and sometimes disappeared from nickel deposits prepared in the presence of DGLP as a brightener. The results of this study show that DGL can be used satisfactorily, with minimum operations as a brightening agent for nickel electrodeposition. The key idea of direct immersion of DGLP in the Watts bath, aimed to the replacement of synthetic brighteners and the reduction of the overall cost of nickel electrodeposition.*

**Keywords:** *Electrodeposition, Nickel, Daphne Gnidium L., Brightners, cyclic voltammetry*

### 1. INTRODUCTION

Electrodeposition of nickel is one of the most intensively studied electrochemical processes, ranging from simple thin films for decorative purposes to corrosion and wear-resistant coatings. Nickel is generally electrodeposited from sulfate or sulfamate electrolytes with or without additives, and also from a Watts-type electrolyte containing nickel sulfate, nickel chloride and boric acid. However, the plating baths contain not only the precursor of the metal to be plated but also additional agents, such as saccharin, glycerol, mannitol, sorbitol and formaldehyde. It is known that organic additives are introduced in trace amounts to the plating solutions to modify the structure, morphology and properties of the deposits. Researching for new additives is therefore of great interest [1-3].

In the case of nickel, additions are made to reduce pitting, increase hardness, remove strains in the deposit, improve corrosion

resistance, fill in macroscopic scratches, and give a mirror-like luster to the surface [4, 5]. The study of the effects of additives on the electrodeposition of the most commonly used metals in metal finishing such as zinc, copper and nickel has led to new insights [4].

In electrodeposition of metals, primary and secondary brighteners are used. Primary brighteners allow secondary brighteners to have higher efficiency and a widened sphere of action [5]. Secondary brighteners are used to achieve the same degree of mirror brightness, but in the absence of the primary brighteners, they can often cause excessive fragility in the deposit [1-5].

In recent years, there has been an increasing awareness of the toxicity of chemical products on both environment and human health. Therefore, many studies have been conducted with the aim of finding a way to replace harmful synthetic chemicals used as corrosion inhibitors by environmentally friendly inexpensive and readily available substances. It is worth mentioning here, that the first corrosion inhibitors used, were extracts from various parts

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(leaves, bark, stems...) of different plants [6-12]. However, only a very few results regarding the use of natural substances as additives for metal electrodeposition have been reported in published literature [13].

Recently, Loto. C. A. studied successfully the synergism of *saccharum officinarum* and *Ananas comosus* extract additives for zinc electroplating on mild steel.

The synthetic coumarin (2H-1-benzopyrane-2-one) was successfully used as an additive to chloride baths or to Watts baths for Zinc and nickel electrodeposition respectively [4, 14-17].

In the present study, the potential replacement of synthetic additives of the Watts bath for nickel electrodeposition, by a plant known to be a rich source of polyphenols, mainly coumarins, *Daphne gnidium* L. [18,19] was investigated to improve the quality of deposits. It's worth noting that we are interested in evaluating the effect of this plant on the brightness of nickel deposits at lower cost. Coumarins of *Daphne gnidium* L. are structurally different from the simple synthetic coumarin because they contain more electron giving groups.

The results of adding to the Watts bath either an accurate amount of dried and powdered plant (DGLP) with no further treatment, or a plant extract (DGLE), were compared to those obtained by using glycerol and formaldehyde as brighteners.

Cyclic voltammetry studies were carried out to investigate the electrochemical behavior of baths and Scanning Electron Microscopy (SEM) was performed to examine the morphological aspects of the nickel deposits. EDS analyses were carried out to evaluate the nickel percentage in the deposits. The brightness of nickel deposits was determined both visually and using a Gloss meter.

## 2. EXPERIMENTAL

### 2.1. Plant specifications

Nickel electrodeposition on copper substrate was studied in the presence of *DGL* leaves, a plant belonging to the thymeleacea family. *Daphne gnidium* L. is native to the Iberian Peninsula, France, the Apennine Peninsula, the Balkan Peninsula, the Canary Islands, Madeira and North Africa [20-22]. *Daphne gnidium* L. is a plant belonging to the genus *Daphn* and species *gnidium*. It is also known as Flax-leaved daphne. It is a mid-sized, evergreen shrub with crowded, narrow leaves. It bears fragrant, white flowers in late spring and early summer. Red fruits appear in autumn. The leaves of *Daphne gnidium* L. have been used in traditional fabric dyeing [23]. This plant is also important for its medicinal uses, it has been reported to have antioxidant [18, 24], and antibacterial [25] properties. In folk medicine, the infusion of the leaves is used as a hypoglycemic agent [26] and as treatment for skin diseases [27].

### 2.2. DGL powder (DGLP) preparation

Leaves of DGL were collected from Guelma region, situated in the northeastern part of Algeria; they were shade-dried at room temperature, for many days, and pulverized using an electric grinder.

DGLP was directly immersed into the Watts bath, where it was allowed to macerate for 24 hours, before filtrating the bath content, used for nickel electrodeposition.

### 2.3. DGL extracts (DGLE) preparation

An amount of 50 g of DGLP were macerated in a solvent mixture

composed of 80/20 %, V/V methanol/water in a closed container at room temperature for 24 hrs. The extract was then filtered and the solid residue was again subjected to extraction using the same solvent mixture. This operation was repeated five times to achieve an exhaustive extraction of all plant secondary metabolites. The extracts were collected and methanol was removed by vacuum evaporation using a rotary evaporator. The aqueous extract was freeze-dried and the obtained powder was used, in various amounts, as an additive to the Watts bath for nickel electrodeposition.

### 2.4. Electrodeposition

Nickel electrodeposition was performed in the Watts bath. The electrolytic bath composition and operating parameters are presented in Table 1. All experiments were carried out at  $58 \pm 1^\circ\text{C}$ . High purity copper substrate sheet (2 cm<sup>2</sup> surface area) was used as a working electrode. A nickel plate (99% purity) having an approximate surface area of 2 cm<sup>2</sup> was used as the anode. Both electrodes were vertically set in the cell with a distance of 2 cm between them. Copper substrates were mechanically polished with abrasive papers of 600 and 1200 grits, then rinsed with distilled water and pickled in 10% H<sub>2</sub>SO<sub>4</sub> solution, rinsed with distilled water and dried at room temperature [28, 29]. Nickel electrodeposition was performed in the Watts bath with synthetic and natural alternative additives used for the electrochemical studies. DGLP and DGLE were consecutively tested as wetting agent, primary and secondary brighteners. Plating assays showed that neither DGLP nor DGLE can be used as wetting agents because the surface of the deposits obtained presented many pits. The different baths used for this study are indicated in Table 2.

### 2.5. Cyclic voltammetry

Voltammetric measurements were performed with a three-electrode cell consisting of a copper substrate (working electrode),

Table 1. Watts bath composition, additives and operating parameters.

Watts bath	
NiSO <sub>4</sub> ·6H <sub>2</sub> O	250 g/L
NiCl <sub>2</sub> ·6H <sub>2</sub> O	45 g/L
H <sub>3</sub> BO <sub>3</sub>	40 g/L
Additives	
Sodium Dodecyl Sulfate (SDS), Wetting agent	1 g/L
Glycerol (Gly), Primary brightener	16 ml/L
Formaldehyde (FA), Secondary brightener	6 ml/L
<i>Daphne gnidium</i> L. powder, DGLP	10 g/L
<i>Daphne gnidium</i> L. extract, DGLE	(0.5, 2.5, 5,7) g/L
Operating parameters	
Current density, j	4 A dm <sup>-2</sup>
Temperature, T	58 ± 1 °C
Time	120 s
pH	3.5

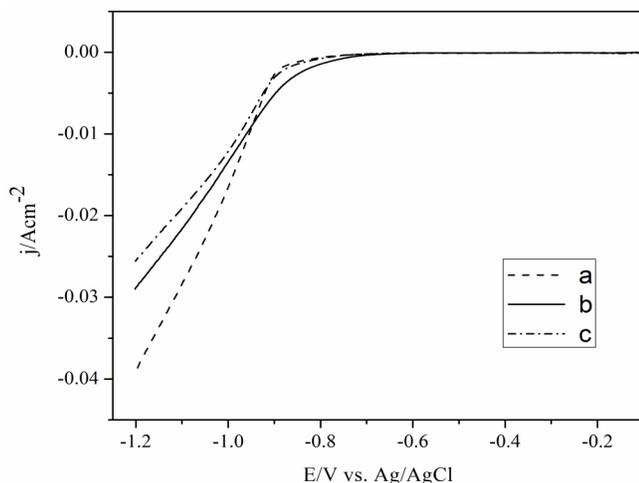


Figure 1. Voltammetric curves obtained on copper electrode at a scan rate of  $20 \text{ mVs}^{-1}$ , in different electrolytic solutions: (a) Watts bath, (b) Watts + SDS, (c) Watts + SDS + Gly.

a platinum plate (auxiliary electrode), and an Ag/AgCl electrode immersed in a separated compartment filled with KCl solution (reference electrode). The scan rate was set at  $20 \text{ mVs}^{-1}$ . Electrochemical experiments were carried out in a conventional three-electrode glass cell using a potentiostat/galvanostat device model 273A (EG & G Princeton Applied Research) controlled by Power Suite software.

## 2.6. Morphological examination

Morphological examination of nickel deposits involved visual inspection and scanning electron microscopy (SEM) observations using JEOL JSM-5600LV SEM.

## 2.7. Gloss measurements

The brightness of deposits was visually estimated, whereas the gloss measurements were performed with a PICOGLOSS 560 MC ERICHSEN micro-gloss meter with an extended beam white light,

Table 2. Baths used for nickel electrodeposition including Watts bath without and with synthetic and natural alternative additives

N°	Watts Bath (W)	Wetting agent	Primary brightener	Secondary brightener
1	W	/	/	/
2	W	SDS	Gly	/
3	W	SDS	DGLP	/
4	W	SDS	DGLE	/
5	W	SDS	Gly	FA
6	W	SDS	Gly	DGLP
7	W	SDS	Gly	DGLE

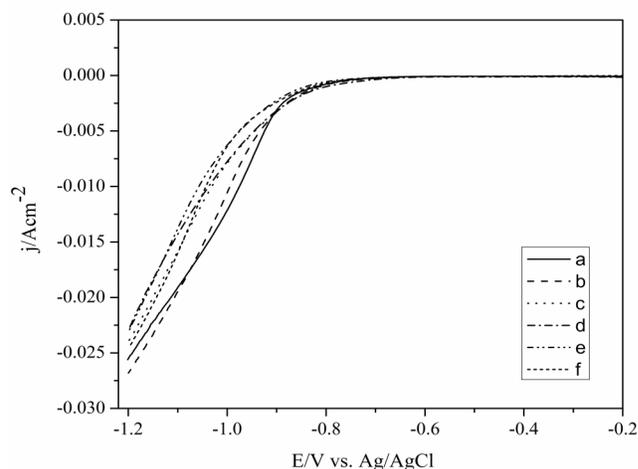


Figure 2. Voltammetric curves obtained on copper substrate at a scan rate of  $20 \text{ mVs}^{-1}$  in different electrolytic solutions: (a) Watts + SDS + Gly, (b) Watts + SDS + DGLE (0.5 g/L), (c) Watts + SDS + DGLE (2.5 g/L), (d) Watts + SDS + DGLE (5 g/L), (e) Watts + SDS + DGLE (7 g/L), (f) Watts + SDS + DGLP (10 g/L).

and a  $60^\circ$  measurement angle. The calibration was performed automatically by means of a highly polished black standard integrated in the gloss meter. The gloss final value is the mean of three measurements performed in triplicate, for each coating.

## 3. RESULTS AND DISCUSSION

### 3.1. Voltammetric study

In this study, three widely used organic additives of the Watts bath for nickel electrodeposition: sodium dodecyl sulfate, glycerol and formaldehyde were substituted by powdered leaves of DGL, with no further treatment (DGLP) and DGL leaves extract (DGLE). The electrochemical behaviors of different baths were investigated by cyclic voltammetry.

A typical voltammogram related to the Watts bath is presented in Fig. 1a. It shows that reduction of nickel ions starts at about  $-0.8 \text{ V}$  leading to the formation of a deposit according to the following reaction:



The voltammograms of the Watts bath without additives and with SDS as a wetting agent and glycerol as primary brightener are shown in Fig. 1. We can see from this figure that glycerol is a better inhibitor for the reduction reaction of nickel ions than SDS.

Fig. 2 illustrates the effects exerted by glycerol ( $16 \text{ mL}^{-1}$ ), DGLP (10 g/L) and DGLE (0.5, 2.5, 5, 7 g/L) as primary brighteners on electrodeposited plates. It can be clearly seen from this figure that DGLE at three concentrations (2.5, 5, 7 g/L) and DGLP have the same efficiency on the inhibition reaction. Both of them are better inhibitors of the  $\text{Ni}^{2+}$  ions' reduction reaction than glycerol. Curves in Fig. 3 illustrate the behavior of the Watts bath in the presence of formaldehyde, DGLP and DGLE (at various concentrations) as secondary brighteners. The inhibitory action of DGLE at three concentrations (2.5, 5 and 7 g/L) and DGLP was found to be

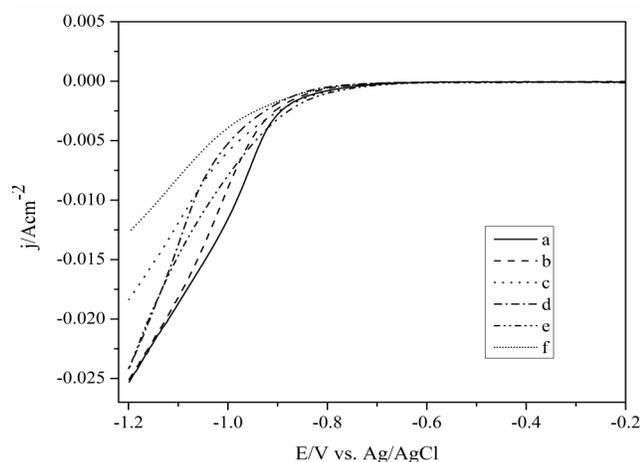


Figure 3. Voltammetric curves obtained on copper substrate at a scan rate of  $20 \text{ mVs}^{-1}$  in different electrolytic solutions: (a) Watts + SDS + Gly + FA, (b) Watts + SDS + Gly + DGLE (0.5g/L), (c) Watts + SDS + Gly + DGLE (2.5 g/L), (d) Watts + SDS + Gly + DGLE (5 g/L), (e) Watts + SDS + Gly + DGLE (7 g/L), (f) Watts + SDS + Gly + DGLP (10 g/L).

higher compared to that of formaldehyde, whereas DGLE at a concentration of 0.5 g/L had lower inhibitory effect than formaldehyde.

Fig. 3 also shows that DGLP has a marked inhibitory action, especially at very cathodic potentials. This effect leads to an increase in the rate of the nucleation process, and hence grain size will be smaller giving a deposit with a smoother surface [30-32]. The role of DGL as an inhibitor of  $\text{Ni}^{2+}$  ions' reduction reaction could be attributed to the chemical compounds present in this plant, especially coumarins [18,19].

These phytochemicals contain electron donating unsaturated  $-\text{O}-\text{C}=\text{O}$  groups [1,16]. The presence of other donating groups such as OH,  $\text{OCH}_3$ , and O-Glucose which are the most frequent substituents found in coumarins of DGL, together with the  $-\text{O}-\text{C}=\text{O}$  group, increases the electron donating capability. A literature search shows that the major compounds of DGL are hydroxy-, methoxy-, and glycosyl-coumarins [18,19] such as daphnin, daphnetin, daphnoretin, acetylumbelliferone, etc. The noticeably inhibitory role given by DGL plant in this study could be due to the co-existence of several molecules bearing electron-donating substituents.

Comparison of the results from Fig. 2 and Fig. 3 shows that when DGLE is used as a primary brightener, the higher the concentration of additives, the higher the inhibition phenomenon. However, an increase in the concentration of the secondary brightener slows down the inhibition reaction. This is in full agreement with what is well known about surface treatment by the electrolytic method [28-32]. Fig. 4 shows that the difference in current densities registered at  $-1.2 \text{ V}$  between DGLP and glycerol is  $\Delta j_1 = 0.00158 \text{ A cm}^{-2}$  and that between DGLP and formaldehyde is  $\Delta j_2 = 0.01245 \text{ A cm}^{-2}$ . This indicates that the use of DGLP as secondary brightener engenders many more modifications than its use as primary brightener.

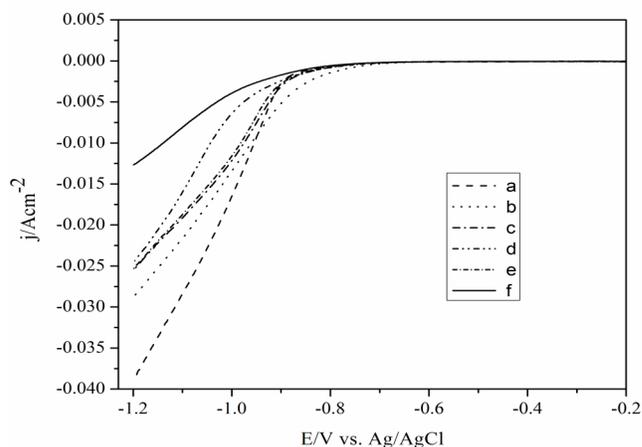


Figure 4. Voltammetric curves obtained on copper substrate at a scan rate of  $20 \text{ mVs}^{-1}$  in different electrolytic solutions: (a) Watts bath, (b) Watts + SDS, (c) Watts + SDS + Gly, (d) Watts + SDS + DGLP (10 g/L), (e) Watts + SDS + Gly + FA, (f) Watts + SDS + Gly + DGLP (10 g/L).

### 3.2. Brightness Study

Since there is no significant difference between nickel inhibition processes by addition of DGLP and DGLE, and because the preparation of DGLP is much more cost-effective than that of DGLE, we limited the study to the effect of DGLP on the brightness of nickel deposits. The results were compared to those obtained with glycerol and formaldehyde. Brightness was first estimated visually, and from the results obtained (Table 3), we can conclude on one hand, that the brightness obtained with DGLP and formaldehyde as secondary brighteners is almost the same and on the other hand, that the brightness of the plates was much better with DGLP and formaldehyde as secondary brighteners than as primary brighteners.

In addition, brightness was measured using a portable microgloss meter PICOGLOSS 560 MC ERICHSEN with a  $60^\circ$  measurement angle. The values obtained were 163 GU, 291 GU and 300 GU, for the Watts bath without additives, with DGLP, and formaldehyde, respectively. This is indicative of a relatively high brightness for the Watts bath with DGLP.

Table 3. Evaluation of brightness of deposits realized in different electrolytic baths

Plating Baths	Brightness
Watts bath (W)	Matt
W + SDS + Gly	Semi bright
W + SDS + DGLP	Semi bright
W + SDS + Gly + FA	Bright
W + SDS + Gly + DGLP	Bright

### 3.3. Morphological study

Surfaces of Ni deposits obtained in the Watts bath with a current density of  $4 \text{ A dm}^{-2}$  containing formaldehyde and DGLP were examined. EDS analyses show that there is no difference in the composition between all deposits studied and the nickel weight percentage is about 95-96 % for deposits obtained in the presence of both synthetic and natural additives. Morphological analyses are presented in Fig. 5. The comparison of the micrographs shows that the Watts bath additives decreased significantly the micro cracks. It also allowed us to draw the conclusion that nickel films obtained in the presence of formaldehyde (Fig. 5 b) and DGLP (Fig.5 c) present a smoother surface compared to that obtained in the Watts bath without additives (Fig. 5 a). These results corroborate those obtained by voltammetric study (3.1).

### 4. CONCLUSION

Based on these results on the study of the influence of a plant powder (DGLP) and extract DGLE) on nickel electrodeposits, it can be concluded that: i)The results obtained with DGLP and DGLE were compared to those obtained with two synthetic brighteners, glycerol and formaldehyde; ii)The voltametric study showed that DGLP and DGLE have an inhibitive effect on reaction of the electrolytic nickel formation and it was attributed to the presence of several polyphenols, particularly coumarins, in DGL.; iii) the evaluation of the brightness and the morphology showed that DGLP might be responsible of the uniformity and the luster of the electrodeposited nickel comparable to those electrodeposited with formaldehyde, a renowned synthetic brightener; iv) it is more advantageous to macerate the plant powder DGLP directly in the Watts bath, rather than using the extracted DGLE organic solvent; v) using DGLP is more economical and less time consuming than using DGLE because the DGLE extraction process is more expensive and involves toxic solvents such as methanol. Moreover, several steps are required, such as maceration, filtration, evaporation, and freeze-drying; vi)The original idea of using pulverized plant directly as a constituent of the Watts bath substantially reduces the overall cost of Ni electroplating while at the same time offering an environmentally friendly substitute to harmful synthetic substances.

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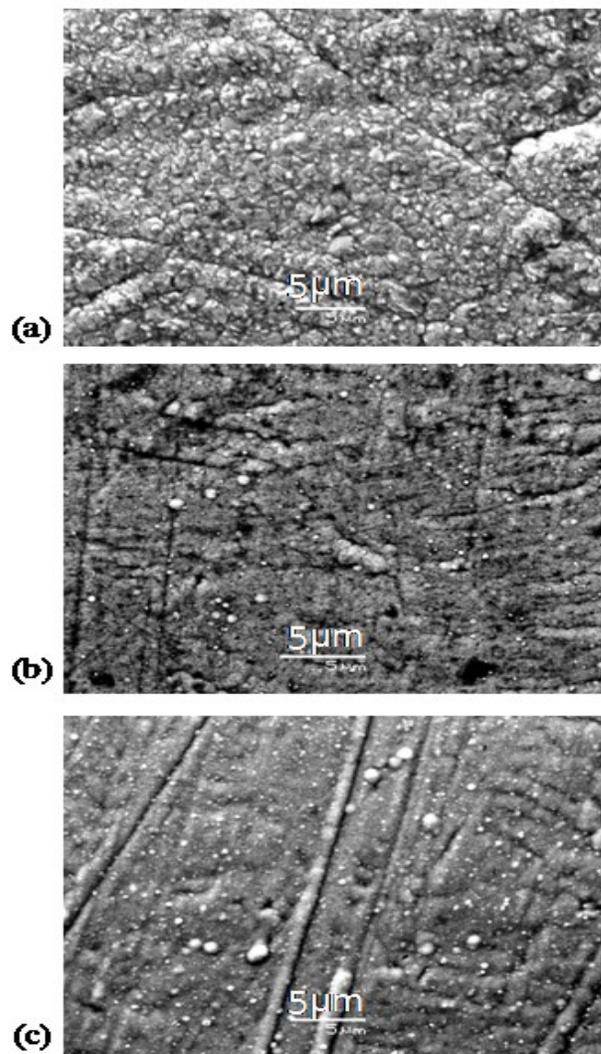


Figure 5. SEM micrographs of nickel coatings obtained on copper substrate with a current density of  $4 \text{ A dm}^{-2}$  and a deposition time of 120 s in different electrolytic solutions: (a)Watts bath, (b) Watts + SDS + Gly + FA, (c) Watts + SDS + Gly + DGLP (10 g/L)

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