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A O Gezerman & B D Çorbacıoglu

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Iron(II) acetylacetonate containing brightener and sulphur containing carrier in nickel plating

A. O. Gezerman* and B. D. Çorbacıoglu

The effects of an iron(II) acetylacetonate containing brightening agent and a carrier on colour and mechanical properties of nickel plating were investigated to determine optimal electroplating process parameters. The brightening agent contained metasulphobenzaldehyde, pyridine-3-sulphonic acid, *p*-vinylbenzenesulfonic acid, *o*-benzoylsulphonamide, sodium saccharine and iron(II) acetylacetonate. The carrier comprised sodium saccharine and sodium allyl sulphonate in water. Plating colour was analysed by visible region spectrophotometry at 350 nm under 6500 K illumination (CIE Standard Illuminant D65). Electron microscopy confirmed that carrier facilitated nickel deposition onto the surface and increased cohesion, thus allowing complete coverage. Moreover, brightening agent increased the bath pH, while carrier did not. In bending experiments on a coated plate, brightening agent increased hydrogen embrittlement, although desired decorative appearance was obtained. Finally, the optimum concentrations of carrier and brightening agent were found to be 12 and 0·4 g L^{-1} respectively.

Keywords: Brightener, Carrier, Acetylacetonate, Embrittlement, Spectrophotometry

Introduction

Various types of plating processes are extensively employed in different industries, both to increase the resistance to corrosion and to impart a more decorative appearance to steel and to metals such as aluminium, zamak and brass. However, the most frequently used plating process is nickel plating.

Electrodeposited nickel is used in various applications such as vehicles and appliances as a decorative yet functional metal coating.[1] Nickel plating, which has been popular in Europe since the 1950s, is now widely accepted in the industry because of the uniformity of the plating and the ease with which complex components can be plated.[2] It is also resistant to corrosion at 20% NaCl concentration, 95% relative humidity and 50°C temperature (according to the ASTM B 117 standard) and has a good level of hardness.

However, when applied to hard and soft metals, nickel plating alone does not produce a distinct decorative appearance or provide corrosion resistance.

The selection of an electroplating bath depends primarily on the required characteristics of the nickel deposit. The sulphamate bath is the most important as it affords plating with low stress and good mechanical properties.[3] However, the process can be expensive and commercially unviable and so, instead, the Watts bath is the most popular. This bath contains boric acid as an essential ingredient for controlling the pH and forming smooth and ductile deposits.[4] However, boron is a harmful substance and has many restrictions on handling and dumping. In addition, strict environmental regulations restricting dumping of wastes containing boron were recently imposed in Japan.[5] Therefore, it seems necessary to find more environmental friendly alternatives to boric acid.

Iron(II) acetylacetonate, citric acid and citrate are chiefly used as pH buffer agents and complexing agents for electroless nickel plating[6] and for electroplating iron alloys,[7] nickel–tungsten alloys[8] and copper–nickel alloys.[9] Acetylacetonate ions react with nickel ions to form nickel acetylacetonate complexes, which are adsorbed on the surface of the cathode. This contributes to the electrodeposition of nickel and the crystallisation of the deposits. Moreover, the acetylacetonate ions remain adsorbed on the cathode surface, thus inhibiting the hydrogen evolution reaction. Hence, iron(II) acetylacetonate could be used as a possible substitute for boric acid.

In addition, the demand for decorative nickel plating has led to novel research on simplification of the process. In particular, brightening agents could be added to control the colour during electroplating itself instead of having to add desired decorative colours after the metal coating for corrosion protection.

Nickel plating has several applications in industry. Previous studies have shown that, among the various metals that can be electrolessly plated, electroless nickel has proved its supremacy for having coatings with high corrosion resistance, hardness, resistance to wearing and uniformity. Electroless nickel can be deposited using a variety of baths and the coat properties depend upon the type of reducing agents and other deposition conditions.[10]

Department of Chemical Engineering, Faculty of Chemical and Metallurgical Engineering, Yildiz Technical University, Istanbul, Turkey

*Corresponding author, email ahmet_ozan@yahoo.com

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The nickel coating mostly used in industry is Ni–P coating, usually obtained using electroless Ni plating baths. There have been many reports on Ni–P plating. In 2009, Rahimi *et al.* tried to increase corrosion resistance at high temperature (400°C) using stabilising agents such as thiurea and lead acetate.[11] In 2009, Choudhury *et al.* tried to perform electroless Ni plating on pure copper (99·99%).[12] Another study reported by Hao *et al.* included Ni–P plating on W–Cu alloy surface where they developed surface features.[13] Except Ni–P, Ni–NCZ plating (electroless nickel plated ZrO_2) was developed by Arghavanian *et al.*[14] Srinivasan and group[15] have reported the development of new bath formulation to obtain Ni–Co–P nanoalloy deposit and optimised bath concentration and operating conditions for another nickel plating bath which formed from Ni–Co and P.

To improve the features of metal surface, in 2009, Ni–W–B alloy was developed by Hosseini *et al.*[16] Also, to improve physical features of nickel plating, in 2011, thermal barrier coating was developed by Wang *et al.*[17]

As for another plating process used in industry, Ni–P–Al_2O_3 process was developed by Rahimi *et al.*,[18] while uniform plating thickness was obtained using titanium powders by Zangeneh-Madar and Jafari in 2012.[19] Moreover, to improve the features of nickel plating surface, Abdeli *et al.* performed Ni–B–Ti coating.[20]

In electroless plating, except of improving of surface features, required features should be ensured possible minimum cost. Therefore, in 2011, Bauri studied NiYSZ plating by adding $AgNO_3$ to nickel plating bath composition.[21] With similar scope, in 2012, Ni–B composition was developed by Ahmadkhaniha and Mahboubi.[22]

Another process of nickel plating using triethoxysilypropyl on microarc oxidised AZ31 magnesium alloy was developed by Chen *et al.*[23]

As passivation process is important in nickel plating baths, in 2011, Wang *et al.* developed electroless Ni–P plating process.[24]

In this study, the effects of iron(II) acetylacetonate in the brightening agent on the amount and thickness of the nickel deposit, and its physical properties were measured using electron microscopy and visible light spectrophotometry. The results of this study may be useful in accelerating the adoption of iron(II) acetylacetonate as a substitute for boric acid.

Experimental procedures

Materials

As mentioned, Watts type baths are used in all nickel processes and their inorganic compositions resemble one another.[6,8] The main composition of the nickel plating bath in our experiments is listed in Table 1, and the analytical results for the bath are listed in Table 2. The composition of the carrier is shown in Table 3 and the composition of the brightening agent is shown in Table 4. The materials for analysis of the bath were 25% ammonia solution (NH_3/H_2O, pH 11·2), 15% potassium chromate solution, murexide indicator, 0·15M EDTA, and 0·2 N silver nitrate. All reagents were obtained in reagent grade from Merck Chemicals (Istanbul, Turkey) and were used without further purification.

Plating experiments

All plating experiments in this study were performed using a Hull cell[25] at 50°C without mixing. As a preliminary step before the experiments, 70 cm^2 (10 × 7 cm) shiny AISI 304 stainless steel plates were exposed to a current of 1 A (0·1 A cm^{-2}) for 10 min in the bath. However, since the plating was not sufficiently thick, a bath with the same chemical composition was used for a second time, but with the current increased to 3 A (0·3 A cm^{-2}) for 10 min. The plates were then cleaned in a degreasing electrolytic bath before plating and were rinsed with tap water. They were then neutralised in a 20% sulphuric acid bath followed by

Table 1 Main composition of nickel plating bath

Material name	Formulation	Concentration/g L^{-1}
Nickel sulphate	$NiSO_4.6H_2O$	260
Nickel chloride	$NiCl_2.6H_2O$	67

Table 2 Analytical results for bath composition

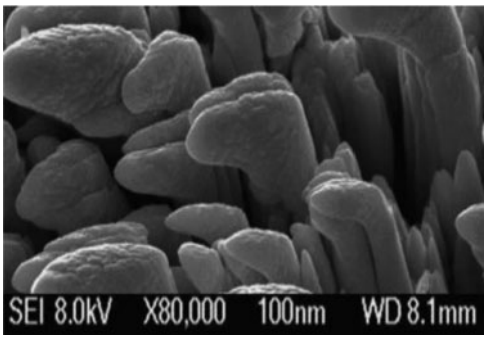
Material name	Formulation	Concentration/g L^{-1}
Metallic nickel	Ni^{2+}	75
Chloride	Cl^-	20

Table 3 Composition of carrier

Material Name	Formulation	For 100 kg of product
Sodium saccharine	$C_7H_4NNaO_3S.2H_2O$	30·0 kg
35% sodium allyl sulphonate	$C_3H_5NaO_3S$	7 kg
Water	H_2O	63 kg

Table 4 Composition of the brightening agent

Material name	Formulation	For 100 kg of product
Metasulphobenzaldehyde	$HSO_3C_6H_5CHO$	8·0 kg
Pyridine-3-sulphonic acid	$SO_2OH_3.C_5H_5N$	4·0 kg
p-Vinylbenzenesulphonic acid	$C_6H_5CHCH_2C_6H_6O_3S$	2·0 kg
o-Benzoylsulphonamide	$C_6H_5SO_2NH_2$	9·0 kg
Sodium saccharine	$C_7H_4NNaO_3S.2H_2O$	20·0 kg
Iron(II) acetylacetonate	$(CH_3COCH{=}C(O)CH_3)_2Fe$	0·5 kg
Water	H_2O	56·5 kg



1 SEM image of nickel plating from bath with no additives

rinsing once again with tap water. The plates were then used in the experiments without being dried. The Hull cell tests were carried out with varying concentrations of the carrier and brightening agent. The quantities of the brightening agent and other compounds were determined in separate instances. To ensure a standard concentration of the various compounds, a large volume of the mixture was used. Thus, the proportions were kept constant, irrespective of the quantity that was added to the bath.

Nickel plating bath analyses

Metallic nickel analysis

Using a pipette, 1 g of sample was transferred from the bath into an Erlenmeyer flask. Next, 100 g of pure water, 10 g of ammonia (25%, pH 11·2) and a small quantity of murexide indicator were added. This was titrated with EDTA until a colour change was observed. The amount consumed multiplied by 5·87 gives the metallic nickel (Ni^{2+}) content in grams per litre.

Chloride analysis

A 1 g sample was pipetted from the bath and transferred into an Erlenmeyer flask. Next, 100 g of distilled water and four or five drops of potassium chromate were added, and the colour changed to crimson red. It was then titrated with silver nitrate until it became reddish brown in colour. The amount consumed multiplied by 3·75 gives the concentration of Cl^- in grams per litre.

Electron microscopy

A Jeol 6060 scanning electron microscope (SEM) was used in secondary electron image mode in this study with the following parameters: resolution, 100 nm; high voltage separation, 8·0 kV, working distance, 8·1 mm, and magnification, 80 000. A total of seven samples from seven different baths were examined: one with the original composition, three with different proportions of carrier and three with different proportions of brightening agent.

Colour analysis

The effect of the brightening agent containing iron(II) acetylacetonate on the colour of the metal plate was examined with the CIE L^*a^*b colour space[26–28] using a visible region spectrophotometer (Macbeth CMC-CE-7000-XL0339) at 325 nm and CIE Standard Illuminant D65, which is equivalent to 6500 K illumination. These values were according to European and Japanese standards. Two different measurements were taken from each plate surface. The colour of each sample was measured twice.

Mechanical hydrogen embrittlement test

The increasing progressive power test method was used to measure the hydrogen embrittlement of the samples. In this method, a force of 14·701 N was applied to a plate that moves progressively between two plates, which is acceptable by the ASTM F519-10 standard.[29]

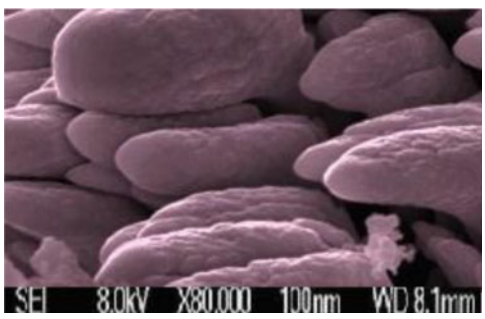
Charpy impact test

For Charpy impact test, ZBC 2000 model device (Sans, China) was used, and according to ASTM E 23 standards, a force of 3 kg cm^{-2} with a fall speed of 5·5 m s^{-1} was applied on metal surface, and adhesion forces were measured on high current density area, which had high coating thickness (10–15 μm) and on low current density area, which had low coating thickness (1–5 μm).

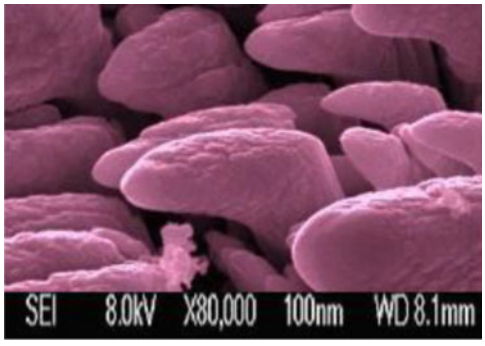
Results and discussion

Effect of additives on colour

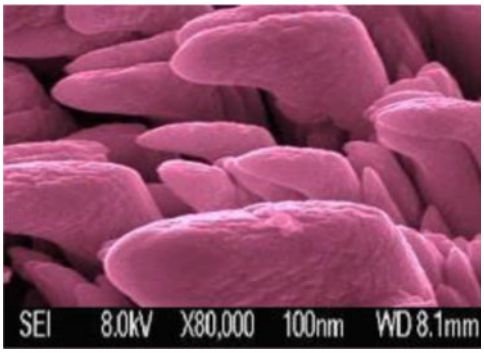
As can be seen from the electron microscope images (Figs. 1–4), the brightening agent produces different shades of red at different concentrations because it contains metallic iron. The concentration of carrier did not affect the nickel coating according to the results of SEM analysis. Under D65 illumination (Figs. 5–7; Tables 5–9), it was observed that the brightening agent plates located on the red side of the red–green axis exhibited an increase in the red axis when the brightening agent concentration is increased. In contrast, during addition of the carrier, the colour does not diverge from the standard (original) bath plate axis. It is observed that the hue (h_0) and chromaticity (c^*) values of the samples do not change much at the point of saturation and a hue of red. Similarly, the L value,



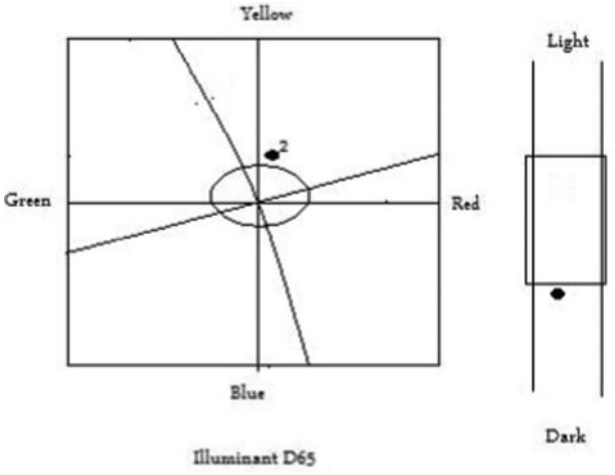
2 SEM image of plating from bath with 0·2 g L^{-1} brightening agent



3 SEM image of plating from bath with 0·4 g L^{-1} brightening agent

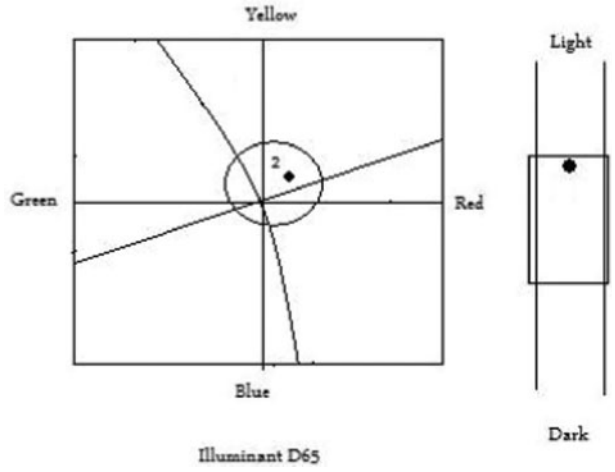


4 SEM image of plating from bath with 0·6 g L^{-1} brightening agent

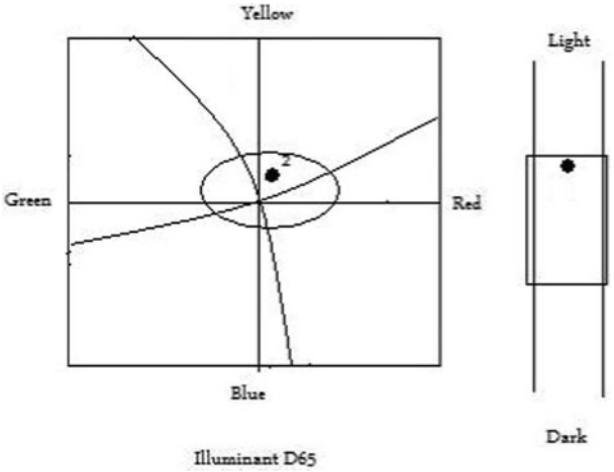


5 Colour measurement of plating from bath with 0·2 g L^{-1} brightening agent: point marked 2 indicates value in second trial

which determines lightness/darkness, does not change with the addition of either agent. Note that in the measurement of the L value, the distance to the standard rectangle located at the middle of the light–dark scale was used as reference.



6 Colour measurement of plating from bath with 0·4 g L^{-1} brightening agent: point marked 2 indicates value in second trial



7 Colour measurement of plating from bath with 0·6 g L^{-1} brightening agent: point marked 2 indicates value in second trial

Optimum additive concentrations

To determine the optimum quantity of carrier to be added by anticipating the quantities that would be required in later experiments, as well as other influences, this amount was set to 10 g L^{-1} and then further increased by 20% to 12 g L^{-1}, which gave a plating with a matte texture.

For the optimum concentration of the brightening agent, it is necessary to consider the effects of pH. An increase in the amount of brightening agent added to the bath leads to an increase in the pH of the bath,[8] which in turn increases the hydrogen embrittlement of the plating. When the metals are plated, cations and hydrogen ions in the buffer solution play an important

Table 5 Colour measurements for plated sample (material) in bath with no additives

Standard	Illuminant	L^*	c^*	h_0
Original bath	D65	19·665	22·630	17·220

Table 6 Colour measurement for 0·2 g L^{-1} brightening agent in bath

Sample (material)	Illuminant	L^*	c^*	h_0
Trial 1	D65	18·331	23·529	19·370
Trial 2	D65	18·221	23·449	19·525

Table 7 Colour measurement for 0·4 g L^{-1} brightening agent in bath

Sample (material)	Illuminant	L^*	c^*	h_0
Trial 1	D65	18·165	23·425	19·445
Trial 2	D65	18·040	23·270	19·632

Table 8 Colour measurement for 0·6 g L^{-1} brightening agent in bath

Sample (material)	Illuminant	L^*	c^*	h_0
Trial 1	D65	18·305	23·372	19·360
Trial 2	D65	18·275	23·292	19·590

Table 9 Results of calculations of differences in the colour measurements

	Trial 1			Trial 2		
Sample (material)	ΔL^*	Δc^*	Δh_0	ΔL^*	Δc^*	Δh_0
0·2 g L^{-1} brightening agent in bath	−1·334	0·899	2·150	−1·459	0·813	2·293
0·4 g L^{-1} brightening agent in bath	−1·444	0·819	2·305	−1·265	0·640	2·412
0·6 g L^{-1} brightening agent in bath	−1·360	0·742	2·140	−1·390	0·662	2·370

role in cohesion to metal surface. So decreasing hydrogen ions in solution results in adhesion problem to metal surface, and increased brittleness.[30] At pH 5·5, cracking occurred 14 h after the test; at pH 6, 13·5 h after the test; and at pH 6·5, 9 h after the test.

The nickel plating bath containing iron(II) acetylacetonate was used for our study Thickness of plating, which is one of the physical properties of metal plating, was measured by X-ray equipment (Fischer Instrument, Germany), while adhesion to metal surface, which is another physical property of plating was measured by Charpy impact test. Charpy impact test showed that coating thickness and adhesion force (cohesion) to metal surface varies in same direction.[31] According to this test, at low current density area where the coating thickness was less, the coating is separated from metal surface due to the impact, but at high current density area, due to stronger adhesion to metal surface, the coating is not separated from metal surface.

A typical Watt bath includes nickel sulphate, nickel chloride and boric acid, and to improve the quality of nickel plating, organic compounds such as brightener and a carrier are used. Boric acid is toxic. In this study, iron(II) acetylacetonate was used, which is as an alternative for boric acid that acts as a buffer antitoxin. Acetylacetonate anion affects the pH of nickel bath similar to boric acid. But, iron(II) acetylacetonate does not have any toxic effect like boric acid. Therefore, iron(II) acetylacetonate can be used as buffer solution.

The effects of iron(II) acetylacetonate on nickel plating bath was investigated using visible region spectrophotometer. When different concentrations of iron(II) acetylacetonate complex were used, different shades of plating were observed on the plated materials. Acidic nature of iron(II) acetylacetonate decreases the pH of brightener solution, but it does not affect the hydrogen embrittlement due to its presence in low concentration, so the optimum concentration of brightener agent, which contains iron(II) acetylacetonate, is 0·5 g L^{-1}. According to this, when the colour of the plated material was investigated on visible region spectrophotometer, desired red colour effect was obtained at 0·4 g L^{-1} of brightener. Further increase in these amounts also increased the hydrogen embrittlement.

For nickel plating process in Watt type baths, current density should be 0·1–0·5 A cm^{-2}.[32] At the current density range, parameters such as uniform spread of nickel plating on materials and chemical consumption need to be detected. Density of 0·3 A cm^{-2} resulted in uniform plating on the metal surface.

Carrier is a component of nickel plating baths. Increasing the amount of carrier does not affect the pH and hydrogen embrittlement. Therefore, in this study, the effects of different amounts of brightener containing iron(II) acetylacetonate were investigated. Other important feature of this study is that a surface plated nickel could be obtained in red, which is generally done by using multiple baths.

Conclusion

In this study, the effects of chemical agents on the physical properties of plating were investigated. It was observed that the carrier facilitated the deposition of nickel and increased cohesion, thus resulting in good coverage. The brightening agent reduced the current efficiency. The brightening agent increased the pH level of the nickel bath, but the carrier did not. It was concluded that the optimum quantity of the carrier was 12 g L^{-1}, and that of the brightening agent, 0·4 g L^{-1}. The optimum process temperature, current density, and plating speed are 45°C–55°C, 0·1–0·5 A cm^{-2} and 0·42 μm min^{-1} (at 0·3 A cm^{-2}). Except the superiority of the physical properties of plated materials, absence of heavy metal, except nickel and absence of toxicity of other chemicals used makes this an efficient method for industry.

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