

Influence of Wetting Additives on the Quality of Nickel Coating

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ABSTRACT

Article Info

Volume 7, Issue 2

Page Number : 15-21

Publication Issue :

March-April-2022

Article History

Accepted : 05 March 2022

Published : 21 March 2022

The paper presents the results of testing the influence of different types of wetting additives on the quality of Ni coating. Three types of additives from three different suppliers were tested under the same conditions at different concentrations. Selected concentrations were: twice lower concentration than lower recommended (C1), lower recommended concentration (C2), upper recommended concentration (C3), twice higher concentration compared to lower recommended (C4), twice higher concentration compared to upper recommended (C5). The surface tension values of the solution were compared and the corrosion resistance in the salt chamber was examined. In addition, what is important in the production itself is the visual appearance of the coating, the comparison of which is also shown in the paper. The obtained results show differences in surface tension, as well as in the visual appearance of the coating. The additive based on C12 - C14 alkyl ether sulfate with essential oils proved to be the most effective in reducing the surface tension of the solution, which results in a much better coating quality as well as aesthetic appearance. The summary results show that the concentration, type and composition of the wetting additive significantly affect the quality of the shiny nickel coating.

Keywords: Electrolyte, Active Substance, Composition, Surface Tension, Coating.

I. INTRODUCTION

Due to the ability to protect technically important metals from corrosion, good mechanical properties and beautiful appearance, nickel coatings are the most important of all metal coatings [1]. Parameters affecting their quality are: composition and type of electrolyte, temperature and time of electrochemical deposition, type of operating electrode, mixing of electrolyte, addition of specific substances to electrolytes known as additives, occurrence of hydrogen evolution as parallel reactions, etc. [2]. Electrolytes used in electroplating are usually of complex composition, because in addition to the metal salts that precipitate, they also contain various specific additives [3]. Additives or specific additives are various chemical compounds, organic or inorganic type, which are added to the electrolyte in order to modify the physical appearance of the coating, its structure, morphology and mechanical properties. The concentration of added additives is quite small compared to the concentrations of other compounds in the electrolyte [4]. The addition of additives also affects the mechanical properties of the precipitated coating [5,6,7], because it changes the structure and mechanism of deposition. All galvanizing baths in their formulation have additives that are used for various purposes such as leveling, grain purification and reduction of internal stress [8]. The addition of organic additives and the presence of impurities in galvanic baths also affects the texture of the galvanic coating [9]. The way in which organic additive affect the properties of electrochemically deposited metal is not always known, and the choice of additive is usually the result of trial and error research method [10]. Modern nickel plating solutions use combinations of additives carefully formulated to create shiny deposits over a wide range of current densities [11]. Wetting additives, so-called surfactants, are used in nickel galvanic baths to ensure complete wetting of parts of the surfaces and to avoid the

development of pores due to hydrogen bubbles. Surfactants are also used as additives to obtain a glossy surface and to control physical coating characteristics such as ductility and hardness [4]. They can also have a negative impact on the characteristics of the layer. Overdose of surfactants can cause unwanted development of foam on the bath surface. Therefore, monitoring the surfactant concentration is necessary for increased process reliability and quality control to ensure the dosing of surfactants according to consumption. In the absence of wetting additive in the nickel deposit, pitting occurs due to trapped hydrogen.

II. EXPERIMENTAL

Several authors [12-19] have documented criticisms of the role of organic additives in the electrodeposition process. The work of a group of authors [20] gives an overview and the role of various organic additives such as brighteners, leveling additives, anti-pitting additives, etc. in the Ni coating bath.

In this paper, the aim was to examine the influence of different types of wetting additives on Ni coating quality, to determine the impact of wetting additive concentration on Ni coating quality, and to compare the visual appearance of Ni coating depending on the type of wetting additives.

III. MATERIAL AND METHODS

For the purposes of the test, a basic solution (Watt solution) was prepared with the prescribed concentrations of the basic additive and gloss additive. The composition of the solution was: NiSO₄ x 6H₂O concentration of 250g/L, H₃BO₃ concentration of 60 g/L, basic additive concentration of 3 ml/L, gloss additive concentration of 1 ml/L. Since a small part of the components was lost by cleaning and filtration, the final analysis of the operating concentrations of

electrolytes was performed by titration, which is shown in Table 1.

Table 1: Operating concentrations in basic electrolyte

Component	Concentration (g/L)
Ni^{2+}	75,71
Cl^-	12,40
H_3BO_3	41,20

The basic solution prepared in this way was used for testing without a wetting additive and then with a wetting additive at five different concentrations. Table 2: Presents composition and concentrations of prepared solutions with the Appendix No.1

Composition (10-30) %	Poly(oxy-1,2-ethanediyl), .alpha.-sulfo-.omega.-hydroxy-, C12-14-alkyl ethers, sodium salts
Active substance	C12 – C14 alkyl ethers, sodium salts
Prescribed concentration (ml/L)	0,8 – 1,0
Concentration of prepared solution (ml/L)	C ₁ = 0,4 C ₂ = 0,8 C ₃ = 1,2 C ₄ = 1,4 C ₅ = 2,0

Table 3: Presents composition and concentrations of prepared solutions with the Appendix No.2

Composition (1-3) %	1.Alcohols, C12–14, ethoxylated, sulfates, sodium salts 2.Sulfuric acid, mono – C12 – 16 – alkyl esters, sodium salts
Active substance	1.Alcohols C12-C14 2.C12 – C16 alkyl esters, sulfuric acid
Prescribed concentration	2,0 – 4,0

(ml/L)	
Concentration of prepared solution (ml/L)	C ₁ = 1,0 C ₂ = 2,0 C ₃ = 4,0 C ₄ = 5,0 C ₅ = 8,0

Table 4: Presents composition and concentrations of prepared solutions with the Appendix No.3

Composition (20-25) %	C12 – 14 alkyl ether sulfate with EO, sodium salt
Active substance	C12 – C14 alkyl ether sulfat
Prescribed concentration (ml/L)	5,0 – 6,0
Concentration of prepared solution (ml/L)	C ₁ = 2,5 C ₂ = 5,0 C ₃ = 6,0 C ₄ = 8,0 C ₅ = 12,0

The surface tension of sixteen prepared solutions of different concentrations (including the basic one without wetting additives) was determined using a hand-held laboratory tensiometer, SITA Dyno tester. pH value was measured using a JUMO pH meter with a combined electrode. A salt chamber: JW - 150 - NS Salt was used to determine corrosion resistance, and the visual quality and presence of pitting was determined using the Hull cell test. A test of *Hull cells* of sixteen prepared solutions (including the basic one without wetting additives) was performed in a Hull cell. The anode and cathode were set to standard, and electrolyte was added after heating. The test was performed on a scratched measuring plate with mechanical mixing at the following parameters: current strength of 2 A, temperature of 55 ° C, pH of the solution 4.0. During the test, the voltage increased to 5.8 V, with no significant changes. Test duration: 10 min. On each of the obtained tiles, one could

visually see the influence of certain types and concentrations of wetting additives.

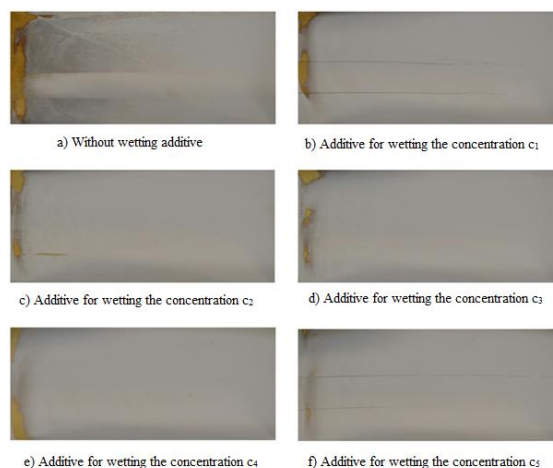
Corrosion resistance was tested on tiles that had a completely covered surface, i.e. tiles with the highest concentrations of additives. Parameters in the salt chamber during the test:

- salt water was prepared using deionized water with a conductivity of $<20 \mu\text{S}/\text{cm}$ and NaCl concentration of $50 \pm 5 \text{ g/L}$
- the temperature in the salt chamber during the test was $35 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$
- pH value during the test was 6,8 (6,5 – 7,2)
- no deviations of parameters in the salt chamber were observed during the test
- after the test, the salt residues from the samples were removed by running water with $T < 40^\circ\text{C}$, and air-dried from the distance of cca 30 cm.

Duration of the test was 48 h [21].

IV. RESULTS AND DISCUSSION

Visual appearance is very important in the quality of the shiny nickel coating because it shows the power of electrolyte application with certain concentrations of wetting additive, there are differences in the visual appearance of the coating depending on the concentration of wetting additive, determining the optimal concentration and type of wetting additive which gives the best efficiency. Tables 5 to 7 present the results of the Hull test cell for the three supplements tested at different concentrations.



Figure

5. Display of Hull plates with Additive based on C12 - C14 alkyl ether, and sodium salts at different concentrations (Appendix No.1)

In the photo shown, it can be seen that the power of application (coating) increases with increasing concentration of the wetting additive. However, even at the highest concentration (2x higher than prescribed) there is partially poor coverage at a part of low current density. Also, the gloss increases over the entire surface of the tile as the concentration of the additive increases, which is most important in the commercial application of glossy nickel plating.

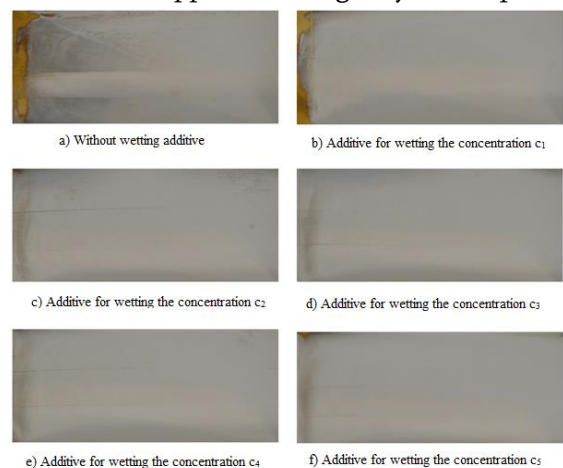


Figure 6.

Display of Hull tiles with Alcohol-based additive C12 - C14, C12 - C16 alkyl esters and sulfuric acid at different concentrations (Appendix No.2)

In the photograph we can see that the power of application (coating) increases with increasing concentration of wetting additive. At the highest concentration (twice the prescribed) there is partially poor coverage at the low current density. Compared

to the additive based on C12 - C14 alkyl ether, and sodium salts, the coverage is much better even at lower concentrations. Also, the gloss increases over the entire surface of the tile as the concentration of the additive increases.

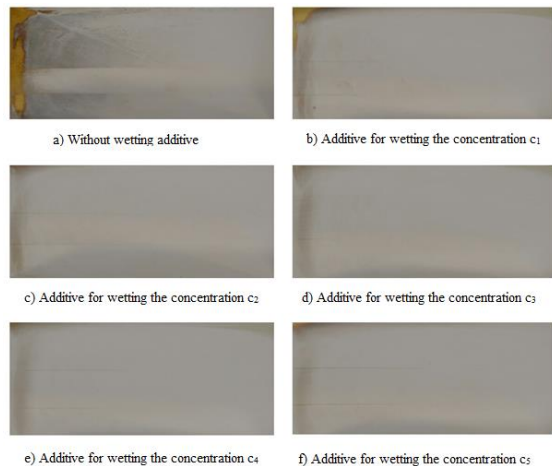


Figure 7.

Display of Hull plates with the additive based on C12 - C14 alkyl ester of sulfate with essential oils at different concentrations (Appendix No.3)

In the photo shown, it can be seen that the power of application (coating) increases with increasing concentration of the wetting additive. Compared to the additive based on C12 - C14 alkyl ether and sodium salts, the coating is much better even at lower concentrations, and compared to the additive based on alcohol C12 - C14, C12 - C16 alkyl esters and sulfuric acid, the coverage is achieved already on concentration that is at the lower prescribed limit (C₂). This shows us that with this supplement we have great efficiency even at lower concentrations.

When measuring the surface tension, the electrolyte temperature was maintained at 55°C, and the procedure was performed according to the instructions of the equipment manufacturer [22]. The obtained results are shown in Figure 8.

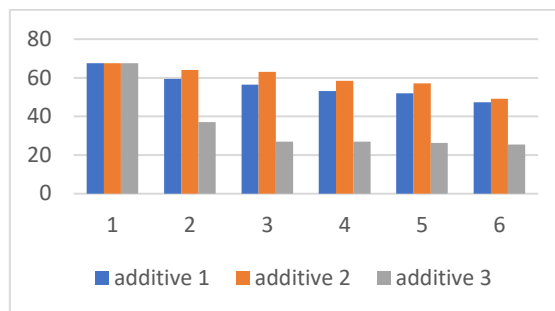


Figure 8.

Comparative presentation of the measuring results of the surface tension of a solution with three different wetting additives

From the presented results it can be seen that the surface tension of the solution decreases with increasing concentration of wetting additive. Surface tension values for the additive based on C12 - C14 alkyl ether and sodium salts range from 59.40 - 47.30 mN/m, for the additive based on alcohol C12 - C14, C12 - C16 alkyl esters and sulfuric acid range in the range of 64.00 - 49.10 mN/m and for the addition to base C12 - C14 alkyl ester of sulfate with essential oils range from 37.10 to 25.50 mN/m. From the presented results it can be seen that the additive based on C12 - C14 alkyl ester of sulfate with essential oils gave the largest decrease in the value of surface tension, and it, in this case, proved to be the most effective.

The results of corrosion resistance measurements in the salt chamber are shown in Figure 9.

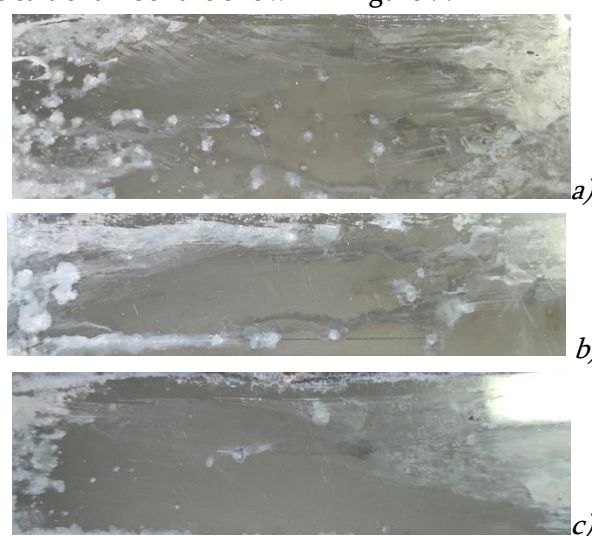


Figure 9. Hull tile a) No.1; b) No.2; c) No.3

During the salt chamber test (Figure 9a, additive based on C12 - C14 alkyl ether, and sodium salts), white corrosion occurred on the tile after 48 h of exposure. Corrosion affected the entire surface of the tile, including areas of lower, medium and higher current densities. During the salt chamber test (Figure 9b, additive based on alcohol C12 - C14, C12 - C16 alkyl ester and sulfuric acid), white corrosion appeared on the tile after 48 h of exposure. Corrosion has mostly affected the area of lower current density, while areas of medium and higher current density are less affected. During the salt chamber test (Figure 9c, additive base on C12 - C14 alkyl ester sulfate with essential oils) white corrosion occurred on the plate after 48 h of exposure. Corrosion affected only the area of medium current density, while the areas of medium and high current density are more stable and without visible corrosion.

V. CONCLUSION

Additive based on C12 - C14 alkyl ether, and sodium salts performs the function when it comes to reducing the surface tension of the solution. Increasing its concentration largely affects the quality of the coating, but even at higher concentrations there was no complete coverage of the tile in the part of low current density ($\approx 0.6 \text{ A/dm}^2$). Additive of alcohol based C12 - C14, C12 - C16 alkyl esters and sulfuric acid also performs a function when it comes to reducing the surface tension of the solution. At higher concentrations, the coating was completely covered, but at a concentration 2x higher than the prescribed one, there was a decrease in the coating power in the part of low current density ($\approx 0.6 \text{ A / dm}^2$).

Additive based on C12 - C14 alkyl ester of sulfate with essential oils has a great power of reducing the surface tension of the solution. Even at low concentrations the surface tension was lower than with the previous two additives at their maximum concentrations.

None of the tested supplements showed the appearance of pitting, which shows that they perform their function successfully, everything else depends on the consumer, and which of them will prove to be the best solution for the procedure used.

When testing the corrosion resistance of the additive based on C12 - C14 alkyl ether, and sodium salts, corrosion affected the entire surface of the tile, including areas of lower, medium and higher current densities.

When testing the corrosion resistance of the additive based on C12 - C14, C12 - C16 alkyl esters and sulfuric acid, corrosion mostly affected the area of lower current density, while the areas of medium and higher current density were less affected.

When testing the corrosion resistance of the additive based on C12 - C14 alkyl ester sulfate with essential oils, corrosion affected only of lower current density area, while the medium and high current density areas were more stable and without visible corrosion.

In the salt chamber test, it can be concluded that the additive based on C12 - C14 alkyl ester sulfate with essential oils is the most resistant, and white corrosion was the least noticeable on the tile with this additive.

The results show that the choice of additives, including wetting additive, is very important during nickel plating. If we work at lower current densities, it would be desirable to use an additive based on C12 - C14 alkyl ester sulfate with essential oils, because it achieves coverage in the area of low current density at already low concentrations. This supplement proved to be the most effective in all parts of the study. The coverage of the surface was the most pronounced, the surface tension the lowest, and the gloss of the tile the most pronounced. If we work at higher current densities, any of the above three additives will be effective, and the decision may be of a purely financial

nature. By using more efficient additives, better results are achieved, and the costs that would be incurred in the event of a poorly done coating are reduced.

VI. REFERENCES

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- [12] Watts and sulfate baths were the most commonly used baths in the nickel electrodeposition process. Brighter nickel surfaces are observed in the presence of propargyl alcohol, propargyl ethoxylate, and propargyl sulfate where dull deposits are obtained in the presence of diethylaminopropane during nickel electrodeposition from a Watts bath.
- [13] The leveling abilities of additives used in the electrodeposited nickel baths have been found to be dependent on cathodic polarization. The additives that increased cathodic polarization have greater leveling performance, whereas the additives that decrease cathodic polarization lead to negative leveling.
- [14] Increases in the temperature and concentration of the organic compound N-allyl quinaldine bromide to 0.1g/dm⁻³ produce increased leveling with a corresponding improvement in brightness compared to other quaternary salts including N-ethyl quinolone bromide and N-propyl quinoline.
- [15] Fine-grained, bright, compact, and smooth nickel electrodeposits are obtained in the

presence of saccharin and its derivatives namely pyridine, 3-, and pyridinium 1-propane 3 sulfonate, and are dependent on the inhibiting effects of these additives on the reduction of nickel ions.

- [16] Aromatic additives benzene sulfonate, benzenedi-sulpahte, benzenesulfinate, and benzenesulfonamide have been used as aromatic brighteners in Watts nickel bath.
- [17] The combination of sodium naphthalene 2-sulfonate and acrylamide additive is used for producing bright, smooth electrodeposits of nickel, where they modify both the structure and the surface morphology of the deposits to a significant extent.
- [18] Saccharin, p-toluene sulfonamide, sodium m-benzene disulfonate, sodium 1,3,5 naphthalene trisulfonate, and O-sulfo benzaldehyde have been described as excellent stress reducers in Watts and sulfate baths for obtaining the desired hardness without tensile stress.
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Cite this article as :

Indira Sestan, Demira Bedak Ogric, Amra Odobasic, Almedin Mujanovic, "Influence of Wetting Additives on the Quality of Nickel Coating", International Journal of Scientific Research in Chemistry (IJSRCH), ISSN : 2456-8457, Volume 7 Issue 1, pp. 15-21, March-April 2022.
URL : <https://ijsrch.com/IJSRCH22721>