

Influence of Wetting Additive Based on C12 - C14 Alkyl Ester Sulphate with Essential Oils on the Quality of Nickel Coating

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ABSTRACT

The influence of wetting additive based on C12 - C14 alkyl ester sulfate with essential oils on the quality of nickel coatings is examined in the paper. The additive was tested at different concentrations added to the base electrolyte, taking the following concentrations: the concentration recommended twice lower (C₁); lower recommended concentration (C₂); upper recommended concentration (C₃); the concentration twice higher compared to the lower recommended (C₄) and the concentration twice higher compared to the upper recommended (C₅). The value of the surface tension of the solution was determined, 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, which was determined using the Hull cell test.

The additive has been proven to be effective in reducing the surface solutions, which directly affects the production of nickel coatings of better quality and aesthetic appearance.

Keywords- coatings, nickel, wetting additive, surface tension

increasingly used in modern industry due to good protective, decorative and technical properties [5].

Nickel coating is similar to other electrodeposition processes using soluble metal anodes; that is, a direct current flows between two electrodes immersed in a conductive, aqueous solution of nickel salt. The flow of direct current causes one of the electrodes (anode) to melt and the other electrode (cathode) to be covered with nickel. Nickel is present in the solution in the form of divalent, positively charged ions (Ni²⁺). When the current flows, the positive ions react with two electrons (2e⁻) and are converted to metallic nickel (Ni⁰). A small percentage of electricity is consumed when releasing hydrogen ions from water. This reduces the efficiency of the nickel deposition cathode from 100% to approximately 96% in an additive-free nickel coating solution. The ejected hydrogen atoms create bubbles of hydrogen gas on the cathode surface. The cathode efficiency of only 90% is characteristic of some glossy nickel covering solutions that are formulated to rapidly yield highly leveled mirror-like layers, i.e. at thicknesses less than 12 μm [6]. Modern nickel coating solutions use combinations of additives carefully formulated to create shiny deposits over a wide range of current densities. These are in fact various wetting improvers to prevent the retention of hydrogen bubbles occurring on the cathode surface (hydrogen is released in parallel with the deposition of nickel due to the high value of the current density of the hydrogen separation on nickel). Aromatic organic compounds are most commonly used. Examples are benzene sulfonic acid, 1,3,6-naphthalene sulfonic acid (sodium salt), p-toluene sulfonamide, saccharin (o-benzoyl sulfonamide), thiophene 2-sulfonic acid, benzene sulfonic acid and allyl sulfonic acid. Carriers are the main source of sulfur applied together with nickel. Their main function is to purify the grain size and create deposits with increased gloss compared to matte or cloudy deposits from baths without additives. When

I. INTRODUCTION

For the most part, the technical problem of preserving various structures from corrosion is solved by separating the base material that has good mechanical properties from the corrosive environment that surrounds it by applying a surface layer, i.e. protective coatings which can be [1,2,3,4]: metal (e.g. nickel, gold, zinc coatings, etc.); non-metallic inorganic and organic coatings. The primary function of all coatings is corrosion protection. The secondary function can be achieving certain physical properties of the surface, protection against mechanical wear, achieving an aesthetic impression, increasing the dimensions of worn parts, or repairing bad products, etc. Nickel coatings are

used alone, the carriers do not create deposits as shiny as a mirror. The end result is a smooth and shiny surface. It follows that lightening is also associated with the leveling action [7]. Coating baths usually contain wetting additives, also known as surfactants. They are characterized by their asymmetry and dipolar nature (\ominus). They have a hydrophilic "head" (\circ) and a hydrophobic "tail". Surfactants can be "anionic", "cationic" or "non-ionic", depending on the charge at the hydrophilic end. Wetting additives are surface-active types, i.e. they act by accumulating on the surface or interface. At the air-electrolyte interface, they are oriented with the hydrophilic head in solution, and with the hydrophobic tail to the air side. In this way, they reduce the surface tension of the liquid [8]. When a surfactant is added to water, the surface voltage drops sharply in order to reach a constant value at a certain concentration value [9]. Anionic or nonionic surfactants are most often used in metal finishing process.

Lowering the surface tension facilitates the release of gas bubbles that adhere to the work surface, whether they are cathodically developed hydrogen or trapped air. In fact, most organic additives, such as the additive tested in this work, act as a hydrogen inhibitor, modifying crystal growth, i.e. their addition is important for the formation of fine-grained, smooth and compact deposits (9). Several authors [10-17] have documented criticisms of the role of organic additives in the electrodeposition process.

II. EXPERIMENTAL PART

The objectives of the experimental work are: to examine the influence of the wetting additive on the Ni coating quality, to determine the influence of the wetting additive concentration on the Ni coating quality and to show the influence of wetting additive on the visual appearance of the coating. In order to determine the effect of wetting additives on electrical deposits, it is assumed that wetting additives have the property of reducing the surface tension of water systems. This in return reduces the interstage tension between the cathode and electrolyte; thus all the hydrogen bubbles that are collected at the cathode are not blinded and forced by the hydrostatic pressure of the electrolyte on the surface of the bath. The result is a smooth, fine grain and a pit-free deposit. For this purpose, the surface tension of the solution was determined using a hand-held laboratory tensiometer SITA Dyno tester. A JUMO pH meter with a combined electrode was used to determine the pH value. A salt chamber JW - 150 - NS Salt Spray Chamber was used to determine corrosion resistance. A Hull test cell was used to determine the visual quality and presence of pitting. For the purposes of the test, a basic solution (Watt solution) was made with the prescribed concentrations of the basic additive and gloss additive. The solution composition is given in Table 1.

Table 1. Basic solution composition

Component	Concentration
NiSO ₄ x 6H ₂ O	250 g/L
NiCl ₂ x 6H ₂ O	60 g/L
H ₃ BO ₃	45 g/L
Basic additive	3 ml/L
Gloss additive	1 ml/L

The basic solution was prepared as follows:

2/3 of the total amount of distilled water was heated to 50°C, and then the salts were dissolved in the following order: H₃BO₃, then NiSO₄ x 6H₂O, and after that NiCl₂ x 6H₂O. After dissolving the salts, the volume was filled up with distilled water. The solution prepared in this way needs to be cleaned of impurities, which is achieved with hydrogen peroxide (30%) and activated carbon. Therefore, 0.5 ml/l H₂O₂ is added to the solution and left to react for 30 minutes. The solution was then filtered through activated carbon at a concentration of 1 g/L. The basic additive and gloss additive were added after the filtration, and the pH was adjusted to 4. Since a small part of the components was lost by cleaning and filtration, the final analysis of the electrolyte operating concentrations was performed by titration, which is shown in Table 2.

Table 2. Operating concentrations in basic electrolyte

Component	Concentration (g/L)
Ni ²⁺	75.71
Cl ⁻	12.40
H ₃ BO 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 3. presents composition and concentrations of prepared solutions with the addition of Crystal Surfact 46M

Composition	%	Active substance
C12-14 alkyl ether sulfate with EO, sodium salt	20 - 25	C12-C14 alkyl ether sulfate with essential oils
Prescribed concentration (ml/L)		Concentration of prepared solutions (ml/L)
5.0 - 6.0		C ₁ = 2.5 C ₂ = 5.0 C ₃ = 6.0 C ₄ = 8.0 C ₅ =12.0

For each of the six prepared solutions (including the basic one without wetting additives), a Hull cell test was performed. The anode and cathode are set according to the standard, and the electrolyte is inserted after heating. The test was performed on a scratched brass plate by mechanical mixing under the following operating conditions: voltage 2 A, temperature: 55°C and solution pH 4. During the test voltage rose to 5.8 V, with no significant changes. Test duration: 10 min. On each of the obtained plates, the effect of the wetting additive in different range of concentrations could be visible to the naked eye.

III. RESULTS AND DISCUSSION

The visual appearance is very important in the quality of the shiny nickel coating, which is one of the main reasons why this method of surface protection is chosen for certain positions. During the operation of the Hull cell, the electrolyte temperature was 55°C, voltage 2 A. Due to the shape of the cell, the plate on which the protection is applied has different current densities along the entire surface, which gives us important information for the nickel coating process.

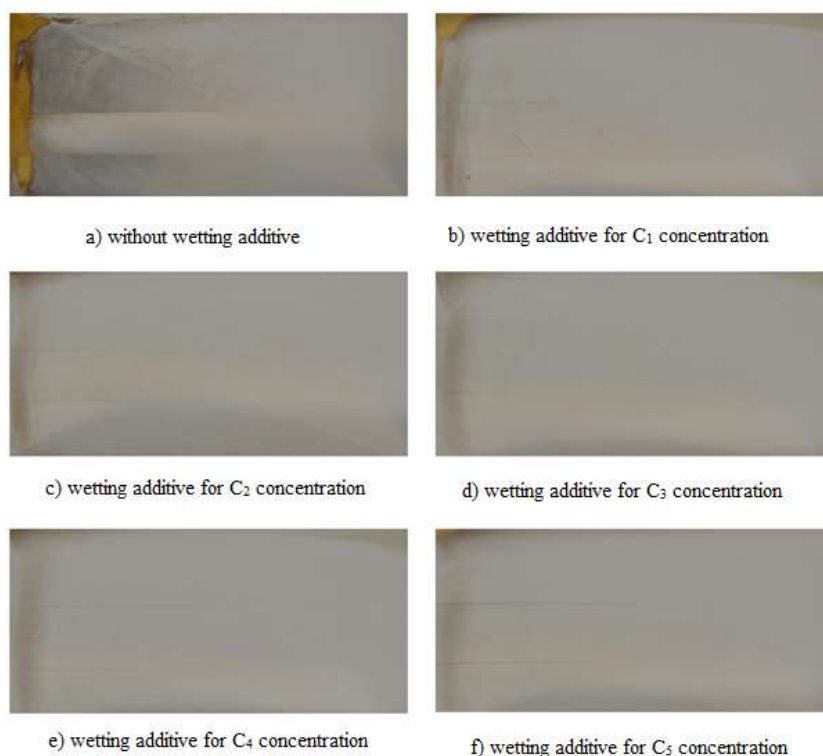


Figure 1: Display of Hull plates with Additive based on a C12 - C14 alkyl ester of sulphate with essential oils at different concentrations

In the photo shown, it can be seen that the application power (coating) increases with increasing concentration of the wetting additive. This shows us that

with this additive there is a great efficiency even at lower concentrations of the additive.

Table 4. provides the results of surface tension measuring of the additive, based on C12 - C14 alkyl ester sulphate with essential oils:

Concentration	Surface voltage (mN/m)	Operating temperature (°C)
C ₀	67.60	55.10
C ₁	37.10	55.10
C ₂	27.00	55.20
C ₃	26.90	55.10
C ₄	26.30	55.80
C ₅	25.50	55.90

From the presented results it can be seen that the surface tension of the solution decreases with increasing concentration of wetting additive. The surface tension values for the C12 - C14 alkyl ester sulphate - based additive with essential oils range from 37.10 to 25.50 mN/m. Thanks to the reduced surface tension, the amount of electrolyte removed from the bathtub by the

wet process is reduced, so there are smaller losses in the electrolyte. The additive based on C12 - C14 alkyl ester of sulfate with essential oils in the electrolyte in the nickel coating process reduced hydrogen embrittlement because there was an increase in surface wettability and thus accelerated separation of hydrogen bubbles from the cathode surface.



Figure 2: The Hull plate with 46M additive after 48 hours in the salt chamber

During the salt chamber test, white corrosion occurred on the tile after 48 h of exposure. The corrosion affected only the medium current density area, while the low and high current density areas were more stable and without visible corrosion.

IV. CONCLUSIONS

1. The additive based on C12 - C14 alkyl ester 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 that of the base electrolyte without the additive, so the tested additive can be used effectively as a wetting additive.
2. The examined additive has not shown the pitting presence, which indicates that it successfully performs its function.
3. When testing the corrosion resistance of the additive based on C12 - C14 alkyl ester sulfate with essential oils, corrosion affected only the area of medium current density, while the areas of low and high current density were more stable and without visible corrosion.
4. The additive used can be recommended as the additive to the base electrolyte in the nickel coating process if a better coating appearance and greater corrosion stability are to be achieved.

REFERENCES

- [1] ASM Volume 13A: Corrosion, fundamentals, testing and protection, ASM International, 2003.
- [2] I. Esih, Z. Dugi: Tehnologija zaštite od korozije I, Školska knjiga, Zagreb, 1990.
- [3] I. Esih: Osnove površinske zaštite, Udžbenici Sveučilišta u Zagrebu, FSB, 2003..5
- [4] D. Jones: Principles and prevention of corrosion, Prentice Hall, 1996.

- [5] Momir Đurović, Goran Radović. Dekorativne i tehničke prevlake nikla – uticaj aditiva i uslova rada. ZAŠTITA MATERIJALA 48 (2007) bro 4, stručni rad.
- [6] Hendricksen, P.C.C.a.H.V., *Trans. Inst. Metal Finish.* 1983.
- [7] Kardos, O., *Proc. Am. Electroplating Soc.* 1956.
- [8] U.S. Mohanty, B.C. Tripathy, P.Singh, Alireza Keshavarz, Stefan Iglauer. Roles of organic and inorganic additives on the surface quality, morphology, and polarization behavior during nickel electrodeposition from various baths: a review. *Journal of Applied Electrochemistry* <https://doi.org/10.1007/s10800-019-01335-w>. REVIEW PAPER.
- [9] S. Gojković. Fizička hemija 2, Površinske pojave. Beograd 2019.
- [10] 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 I sulfate where dull deposits are obtained in the presence of diethylaminopropane during nickel electrodeposition from a Watts bath.
- [11] 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.
- [12] Increases in the temperature and concentration of the organic compound N-allyl quinoline bromide to 0.1 g/dm⁻³ produce increased leveling with a corresponding improvement in brightness compared to other quaternary salts including N-ethyl quinoline bromide and N-propyl quinoline.
- [13] 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.

[14] Aromatic additives benzene sulfonate, benzenedisulphate, benzenesulfinate, and benzenesulfonamide have been used as aromatic brighteners in Watts nickel bath.

[15] 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.

[16] 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.

[17] Several organic additives such as coumarin, adiponitrile, saccharin, and 8-quinoline decrease the leveling action at lower pH in both sulfate and sulfamate bath.