DOI 10.17580/cisisr.2020.01.14

DURABLE LIGHT-ABSORBING COATINGS FOR STRUCTURAL STEELS

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Key words:

electroplating of metals, black nickel coatings, light-absorbing coatings, black nickel, solar receivers, wear-resistant coatings, nickel plating.

ABSTRACT

A black nickel plating process has been developed to install highly durable, adhesive and protective coatings on the following steel grades: 50A and 50RA, 09G2S, Steel 20, Steel 30, 08Kh17.

Nickel sulphate electrolyte with the following composition was used as the base solution (g/L): $NiSO_4 \cdot 7H_2O$ — 100; $(NH_4)_2SO_4$ — 15; $ZnSO_4 \cdot 7H_2O$ — 40; NH_4CNS — 15; H_3BO_3 — 25, at pH = 4.5–5.5, temperature — 50 °C. The following process conditions are associated with the widest current density range (0.1 to 3.0 A/dm²) for black coatings: zinc sulphate concentration — 30–50 g/L, ammonium thiocyanide concentration — 15–20 g/L, pH — 4.5 to 5.5, temperature — 45 to 50 °C. However, such coatings are less protective or durable than black chromium coatings.

A two-stage current mode has been selected to produce black coatings: Stage I — During the initial 10 minutes the current density is slowly increasing from i_1 = 0.02 A/dm² to i_2 = 0.2 A/dm², Stage II — the current density is drastically raised to i_3 = 1.5 A/dm², and the process continues for 10 more minutes. During Stage I, when the current densities are relatively low, an interlayer of light nickel is deposited ensuring good adhesion to the substrate. During Stage II, when the current densities are higher, a black coating is formed of up to 1 μm thick, which consists of metallic nickel and zinc, as well as nickel and zinc sulphides. It is demonstrated that black coatings form due to a drastic rise in zinc concentration in the coating, as well as to the development of roughness caused by current surge.

It is shown that the resultant black nickel coatings are not only comparable with but they can also outperform black chromium coatings in terms of protective capacity and durability.

Introduction

Black electrodeposited coatings are used as light absorbers in optics (Steel 20, Steel 30) and collectors (09G2S) converting the energy of light into thermal energy. They are also used as protective and decorative coatings on furniture fittings (08Kh17), weapons parts (50A and 50RA) et al. [1–3]. The most common types of coatings for the above applications include black chromium and nickel coatings [4–10]. The well-known drawbacks of chromium plating processes include difficulty of implementation and control, as well as high power consumption. The latter is attributed to the need to heat up the solutions, as well as the heat losses related to the hydrogen release by-reaction. Chromium coatings take three times more power than other types of electrodeposited coatings. Besides, chromium coatings fail to properly protect steel from corrosion due to high porosity and internal stresses which lead to cracking [1].

The known black nickel plating processes are less energy intensive and simpler to implement. At the same time, they have a number of drawbacks, which include poor protective capacity, durability and adhesion to the substrate (especially in the case of steel substrate). In black nickel plating, the actual black coating is deposited over a pre-installed copper or satin nickel interlayer. The black coating consists of zinc and nickel sulphides and hydroxides dispersed in metallic nickel. The thickness of such coatings do not exceed 0.5–1.0 μm, and their corrosion resistance is defined by the corrosion resistance of the sublayer [3–5].

This research is aimed at developing an electroplating process to produce nickel coatings with high protective capacity for steel substrates.

Experimental Procedure

2×5 cm steel plates of the following steel grades were used as specimens: 08Kh17 (furniture fittings), 09G2S (solar collectors), Steel 20, Steel 30 (optics), 50A, 50RA (gun steel).

The solutions were prepared with the 'ch' and 'chda' grades of chemical agents and distilled water.

A Hull cell was used as a quick testing tool to evaluate the coating quality on the basis of current density and how the latter would change as a result of changing solution composition or process parameters. The cathode current was 1.0 A [11].

The coating porosity was evaluated for conformance with GOST 9.302-88 (Item 4) by applying filter paper soaked with the solution containing 5 g/L of NaCl and 10 g/L of potassium hexacyanoferrite (III).

A multifunctional thickness gauge *Konstanta K6G* was used to measure the thickness of the coatings.

Durability was tested with the help of Elcometer 5135 Taber Rotary Abraser. Flat coated specimens were mounted to the arms and pressed against the felt wheel, with both arms being subjected to an equal external stress of 3.5 N/cm². The speed of the felt wheel during the abrasion test was 60 rpm. The abrasion resistance of the specimens was evaluated based on the number of revolutions until the coat thickness would reach zero [12].

A salt spray chamber Ascott S450iP (UK) was used to test the specimens for corrosion per ASTM B117.

The elemental composition of black nickel coatings was analyzed on an energy dispersive X-ray fluorescence spectrometer EDX-7000 by Shimadzu (Japan).

XPS spectra were captured with a special camera CLAM100 mounted on an HB100 Auger microscope by Vacuum Generators (GB). As a result, summary spectra of the coatings were obtained which were sorted out into elemental spectra after linear background subtraction [13].

An FM-59M photometer was used to measure the solar reflection factor of the specimens with coatings. The solar absorption factor α_s was calculated with the help of the following formula: $\alpha_s = 1 - \rho_s$, where ρ_s — solar reflection factor.

The coating surface morphology and roughness were studied with the help of a MPLAPONLEXT 100 objective on a laser confocal microscope LEXT–OSL 4100. To analyse the layer structure and surface development, surface images were captured of the same specimen at different stages of surface treatment and after the coating had been formed. 2D and 3D measurements were taken.

Results of Experiments and Discussion

Nickel sulphate electrolyte with the following composition was used as the base solution (g/L): $NiSO_4 \cdot 7H_2O$ — 100; $(NH_4)_2SO_4$ — 15; $ZnSO_4 \cdot 7H_2O$ — 40; NH_4CNS — 15; H_3BO_3 — 25; pH = 5.0, temperature — 50 °C [4].

Through experiments it was established that, in these conditions, the widest current density range (0.1 to 3.0 A/dm²) for black coating deposition can be achieved at the zinc sulphate concentration of 30–50 g/L (**Fig. 1, *a***) and the ammonium thiocyanide concentration of 15–20 g/L (**Fig. 1, *b***). The following ranges proved to be optimum to obtain quality black coatings: pH — 4.5 to 5.5, temperature — 45 to 50 °C. Outside the above pH range the coatings would either fail to form or would not be black. A 45 to 40 °C drop in the temperature of the solution would result in a less deep colour and a tighter current density range — i.e. 0.4-2.6 A/dm². It should be noted that similar results were obtained for all studied steel grades.

The studied solution helped obtain black nickel coatings. However, the tests showed that such coatings are inferior to black chromium coatings in terms of both protective capacity and durability (**Table 1**).

The authors looked at the possibility to improve the above characteristics by changing the current mode during electroplating — for instance, by applying two-stage

Table 1. **Durability and protective capacity of the coatings**

Characteristics	Black Coating	
	Ni	Cr
Durability (number of the wheel revolutions till complete wear), no. of revolutions.	3 000	13 000
Protective capacity (time before the first signs of corrosion on the steel substrate), hours.	50	120

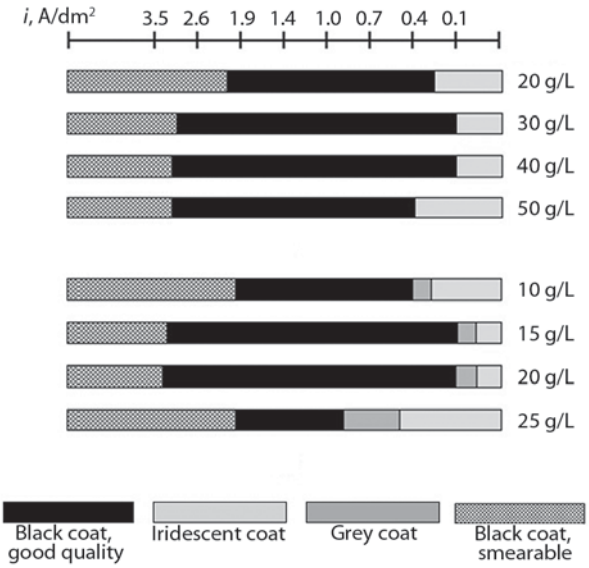


Fig. 1. Hull cell cathode deposit quality as a function of different concentrations of zinc sulphate (*a*) and ammonium thiocyanide (*b*) in the electrolyte: $NiSO_4$ — 100 g/L; $(NH)_4SO_4$ — 15 g/L; H_3BO_3 — 25 g/L;
a — NH_4CNS — 15 g/L; *b* — $ZnSO_4$ — 40 g/L; Temperature — 50 °C; pH = 4.5–5.5

deposition with different current densities at each stage. This electroplating technique involves deposition of an interlayer of light nickel and then a black coating from the same electrolyte by changing the current density. The idea is that during Stage I — i.e. at relatively low current densities — a layer of light nickel is installed that ensures adhesion to the substrate, and then, at higher current densities, a black coating is formed on top [14].

The current modes selected for this study were as follows: during the first 10 minutes of the process the current density would be slowly increasing from $i_1 = 0.02$ A/dm² to $i_2 = 0.2$ A/dm²; after that it would surge to $i_3 = 1.5$ A/dm², and the process would continue for 10 more minutes.

The authors determined the thickness and porosity of black coatings that became the result of single-stage deposition from the base electrolyte at the constant current density of 0.5 A/dm² (referred to as Ni_1) and of those that became the result of dual-stage deposition (referred to as Ni_2) when the current density would be changed as described above. It was established that the thickness of the resultant black coatings Ni_1 and Ni_2 is 2 μm and 1 μm and the porosity is 3 pc/cm² and 1 pc/cm², correspondingly. It was established that the presence of a 10 μm nickel sublayer installed from Watts electrolyte would be sufficient to ensure zero porosity of the total coating (with the black Ni_2 layer), whereas for Ni1 such sublayer should be at least 30 μm thick.

We modified both electroplating techniques to use them for barrel plating of small parts. For this the plating time was extended by 2.5–3.0 times and the current density was increased by 10 % as compared with the rack plating technique.

Table 2. **Solar absorption factors**

Coating	Ni_1	Ni_2	chem. Ni	Cr	Co	Ni–Cu Alloy	Chromate coatings	Molybdate coatings
α	0.91	0.92	0.98	0.95	0.96	0.94	0.93	0.85

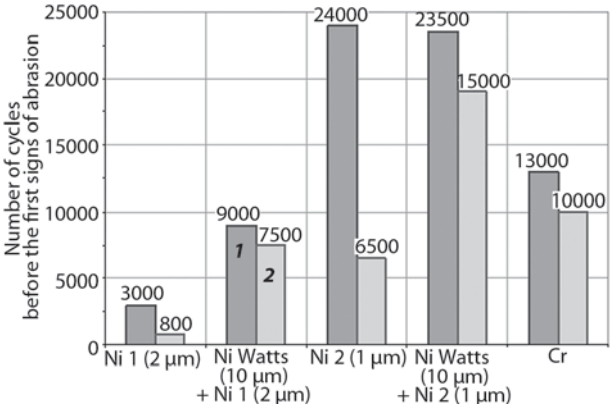


Fig. 2. Abrasion resistance of the coatings (*1* — plating racks; *2* — barrel)

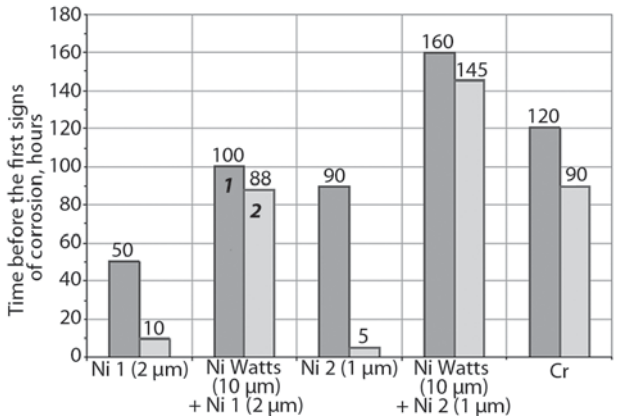


Fig. 3. Time before the first signs of corrosion, hours (*1* — plating racks; *2* — barrel)

Table 2 shows the solar absorption factors of the Ni_1 and Ni_2 coatings, as well as other black coatings that are currently used [3,10,15].

From the above table one can see that the black nickel coatings have similar absorption factors (0.91 and 0.92), and they are comparable to other black coatings from the table.

The results of abrasion tests are shown in the chart (**Fig. 2**). As expected, the durability of the black nickel coating Ni_1 is quite low — 3,000 revolutions of the wheel before full wear. One can see that a common nickel sublayer installed from Watts electrolyte would help increase the durability of these coatings to 9,000 revolutions. This can probably be explained with the fact that the black layer has better adhesion to the nickel base compared with the steel one. The presented data indicate that the durability of the black nickel coatings installed by multi-stage deposition is much higher than that of black chromium coatings or black nickel coatings installed with the help of the original process.

In all cases, the black nickel coatings barrel plated on small steel parts have lower abrasion resistance than the coatings produced on plating racks. This difference is even more pronounced in the case of nickel coatings produced by dual-stage deposition. Such low abrasion resistance of the Ni_2 barrel plated coatings can probably be attributed to the fact that at low current densities parts inside the barrel start to corrode before the coating is formed. The presented data show that this problem can be eliminated with the help of a nickel sublayer installed from Watts electrolyte.

Salt spray chamber tests showed that the time before the first rust spots appeared on specimens with the black nickel coating Ni_2 is 90 hours, whereas for Ni_1 specimens it is only 50 hours (**Fig. 3**). As one would expect, the coatings barrel plated on small parts have a poorer protective capacity than the coatings produced on plating racks. It should be noted that for both electroplating techniques a common nickel sublayer installed from Watts electrolyte can help make the total coating approximately 1.5 times more protective.

Through X-ray fluorescence spectroscopy, it was found that the forming black coatings Ni_1 and Ni_2 mainly consist of zinc, nickel and sulphur (**Table 3**). It should be noted that the coatings produced by staged deposition contain approximately half as much nickel and twice the amount of zinc than the coatings produced in one stage. Both types of coatings contain almost the same amount of sulphur.

The obtained X-ray photoelectronic spectra helped determine the compounds in which the analyzed elements are present in the coating. It was established that the coating is mainly comprised of metallic nickel and zinc and nickel and zinc sulphides.

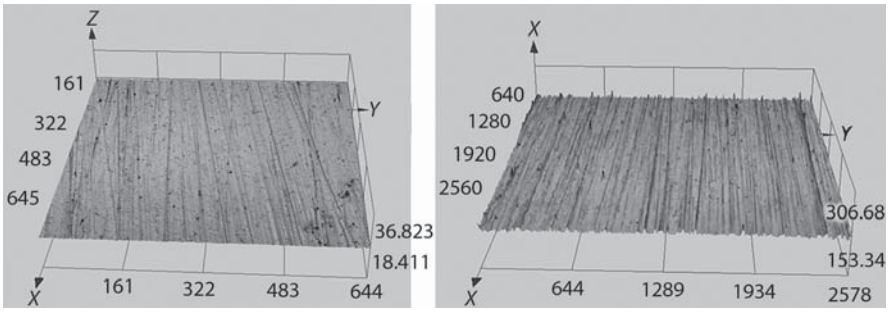
With the help of X-ray fluorescence spectrometry, the authors examined how the changing current mode changes the concentration of nickel in the coating during its staged deposition (**Table 4**). Thus, it was found that it is predominantly nickel that precipitates at low current densities, i.e. during Stage I. As the current density slowly rises during Stage I from 0.02–0.04 A/dm² to 0.2–0.4 A/dm², the nickel concentration increases from 46 to 66%, whereas the concentration of zinc drops from 20 to 15%. After the current density has jumped to 1.5 A/dm², the

Table 3. **X-Ray fluorescence analysis data**

Coating	Component concentration, %		
	Nickel	Zinc	Sulphur
Ni_1	58	30	12
Ni_2	28	59	13

Table 4. **Ni_2 coatings: X-ray fluorescence analysis data**

Current density, A/dm²	Component concentration, %		
	Nickel	Zinc	Sulphur
0.02–0.04	46	20	34
0.2–0.4	66	15	19
1.5	28	59	13



a *b*

Fig. 4. 3D photos of the black nickel coating surface (*a* — Ni_1; *b* — Ni_2)

concentration of zinc sees a drastic rise to 59%, whereas the concentration of nickel drops to 28%.

Apparently, the observed effects can be linked to the changing precipitation potential. As the standard reduction potential of Ni^{2+} is approximately 0.5V more positive than the reduction potential of Zn^{2+}, at lower current densities and, correspondingly, lower potentials it will mainly be nickel that will precipitate, whereas at higher currents and, consequently, potentials we should expect to observe a predominant precipitation of zinc [14].

Roughness tests showed that a coating deposited at low current densities (0.2–0.4 A/dm²) has the roughness of Ra = 0.053 μm; during Stage I the roughness increases some and shortly before the current surge Ra = 0.086 μm. After the current surge the roughness rises by 26 times reaching 2.233 μm. We should note that the coating Ni_1 has a low roughness: Ra = 0.262 μm. The difference in roughness between the coatings produced by the two techniques is shown in 3D photos in **Fig. 4**.

It is well-known that at high Ra light absorption prevails over light reflection, while specular reflection is completely substituted by diffuse scattering [16]. As a result of such optical phenomena, the coating looks like a matte black coating, which is due to light absorption by rough surface.

Conclusions

A black nickel plating process has been developed to install highly durable, adhesive and protective coatings on steel substrate with the help of plating racks and in the barrel from a sulphate electrolyte containing (g/L): $NiSO_4 \cdot 7H_2O$ — 100; $(NH_4)_2SO_4$ — 15; $ZnSO_4 \cdot 7H_2O$ — 40; NH_4CNS — 15; H_3BO_3 — 25, at pH = 4.5–5.5, temperature — 50 °C.

A two-stage current mode has been selected: Stage I — the current density is slowly rising from i_1 to i_2 in the time τ_1; Stage II — a drastic rise in the current density to i_3 for the time τ_2. This current mode enables to form black coatings 1 μm thick comprised of metallic nickel and zinc, as well nickel and zinc sulphides.

It is demonstrated that black coatings form due to a drastic rise in zinc concentration in the coating, as well as to the development of roughness caused by current surge.

It is shown that the resultant black nickel coatings are not only comparable with but they can also outperform black chromium coatings in terms of protective capacity and durability.

It was established that black coatings electrodeposited on steel substrates of the following grades: 50A and 50RA (weapons), 09G2S (solar collectors), 08Kh17 (furniture fittings), Steel 20 and Steel 30 (optics) — have similar durability, protective capacity and absorption factor.

This research was funded by D. Mendeleev University of Chemical Technology of Russia. Project No. 016-2018.

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