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Development of Recycling Technology for Spent Chemical Nickel Plating Solution

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Abstract

Currently, the chemical nickel plating process is one of the most popular electroplating methods compared to others due to a number of advantages. However, the production process generates a significant amount of spent chemical nickel plating solutions, which poses a threat of environmental pollution. To solve this problem, the possibility of regenerating the spent solution of chemical nickel plating from one of the industrial enterprises of Udmurtia by the reagent method was studied. Sodium carbonate was chosen as the precipitant for nickel ions, the amount of which was determined from potentiometric titration curves; the most complete precipitation of nickel ions occurs at pH 10. It has been established by IR spectroscopy that nickel hydroxide salts are formed as a result of the interaction of the spent electrolyte with the precipitant. The results of thermogravimetric and differential thermal analysis of the precipitate showed three endothermic effects: at temperatures up to 100 °C, it corresponds to dehydration; at 280±10 °C – to the removal of a part of chemisorbed water and carbonates; at 420 °C – to the final removal of water. As a result of heat treatment of the hydroxocarbonate precipitate, a black fine powder of nickel(II) oxide is obtained, the IR spectrum of which has a set of bands characteristic of this compound. Two variants of the technological scheme for the regeneration of spent electrolytes for the preparation of initial working solutions for chemical nickel plating from nickel(II) hydroxocarbonate and nickel oxide are proposed. The quality of the obtained solutions was checked by applying a nickel coating on brass products. The thickness of the coating was measured by scanning electron microscopy. It has been established that the highest quality coating is obtained using an electrolyte prepared from nickel hydroxocarbonate.

Keywords: spent chemical nickel plating solution, disposal, nickel compounds, IR spectra, thermogravimetric analysis, differential thermal analysis, coating thickness

INTRODUCTION

Chemical nickel plating is widely used in machine building enterprises in Russia because this allows obtaining a coating that possesses a number of valuable properties: uniformity, hardness, wear resistance [1]. One of the most essential nickel compounds in high demand is nickel(II) hydroxide, which is used to manufacture storage batteries, nickel-containing catalysts, as pigments for glass and ceramics, to obtain nickel salts, in electrical engineering, electrochemistry and radio engineering industry, as a component of the charge in the production of coloured ceramics [2].

However, chemical nickel plating has a substantial drawback – high process cost due to a short lifetime of nickel plating solutions. The spent solutions from chemical nickel plating (SSCN) are liquid wastes. As a rule, at present, SSCN are stored at the territory of enterprises. This not only brings the danger of environmental pollution, but also leads to the loss of valuable and not

readily available nickel compounds, which may be considered as a secondary material resource [3]. To solve this problem, a concept has been developed [4] to recover nickel from SSCN using the reagent method of processing, followed by neutralization of the residual solution with a small concentration of the heavy metal according to the known reagent-based technology.

The goal of the present work was to study the possibility and to develop the technological flowchart of the regeneration of spent solutions from chemical nickel plating by the reagent method in order to obtain initial working solutions.

EXPERIMENTAL

To investigate the treatment of the liquid waste from galvanic productions, SSCN from one of the industrial enterprises of Udmurtia was involved. The composition of the initial working solution is presented in Table 1.

The necessary amount of the 10 % sodium carbonate solution required to precipitate Ni^{2+} ions in SSCN was calculated from the curves of potentiometric titration, which was carried out with a laboratory ion meter I-160MI (Russia) with glass (ES-10603) and silver chloride (ESr-10103) electrodes. The residual content of metal ions in the solution was determined by trilonometric titration in the presence of murexide [5]. The degree of nickel ion recovery (DR, %) was calculated according to the equation:

$$\mathrm{DR} = \frac{C_{\mathrm{in}} - C_{\mathrm{res}}}{C_{\mathrm{in}}} \cdot 100$$

where C_{in} and C_{res} are initial and residual nickel(II) concentrations in the sample, respectively.

Nickel compounds formed during deposition were identified by means of IR spectroscopy. The spectra were recorded with a FSM 1202 IR Fourier spectrometer (Russia) within the region 400–4000 cm^{-1} with respect to air with the resolution of 1 cm^{-1} and summing over 16 scans. The samples under study were prepared to measurement by manufacturing the tablets by pressing a mixture of 1 mg of the deposit and 250 mg of KBr (specially pure reagent grade).

TABLE 1

Composition of the working solution from the galvanic productions of nickel plating (pH 4–5)

Component	Content, g/dm^3
$NiSO_4$	20–30
NaH_2PO_3	25–30
CH_3COONa	10–15
CH_3COOH	5–10
$CS(NH_2)_2$	0.001–0.0005

Thermal studies were carried out by means of thermogravimetric (TGA) and differential thermal analysis (DTA) with a synchronous analyzer Shimadzu DTG-60H (Japan). Thermograms were recorded within the temperature range 25–500 °C at the heating rate 5 °C/min.

Preparation of the samples with the deposited nickel coating was carried out with a SEMPrep 2 set-up (Technoorg Linda Ltd., Hungary) by making an oblique cut at an angle of 30° to the sample surface with the help of Ar^+ ions. The incident beam energy was 10 keV, beam current was ≈250 μA. The thickness of nickel coating in the oblique cuts was studied by scanning electron microscopy (SEM) with the help of a scanning electron microscope Quattro-S (Thermo Fisher Scientific, USA) with the resolution of 0.8 nm.

RESULTS AND DISCUSSION

According to the literature data [6, 7], it is possible to carry out SSCN processing using several methods: ion exchange, electrolytic, and reagent-based. We chose the latter because the reagent method of SSCN utilization is distinguished by the simplicity of instrumentation and economic efficiency. Sodium carbonate was used as a precipitating agent because its application allows us to isolate Ni^{2+} in the form of hydroxide, a compound with one of the lowest solubility limit values for this ion [8], used further on to recover the initial electrolyte. It is also known [9] that nickel hydroxide is used as a pigment in ceramic, glass and paint-and-varnish branches of industry. It should be stressed that the interaction of nickel sulphate with sodium carbonate leads to the formation of nickel hydroxocarbonate with variable composition, with the ratio $Ni(CO_3)/Ni(OH)_2$ equal to 0.05–5 depending on the conditions [10]. According to [11], nickel hydroxide and basic salts form layered structures with strong interatomic bonds within the layer and weak bonds between the layers.

The process of nickel precipitation with sodium carbonate depends on a number of factors: solution acidity (pH), order of reagents mixing, the rate of precipitating agent supply, and mixing intensity. It has been established [12] that pH plays a substan-

tial part in the completeness of nickel ion precipitation.

The presence of phosphites and acetic acid, the components reacting with sodium carbonate, in SSCN excludes the possibility of calculating the reagent amount necessary for complete precipitation of nickel ions in the form of hydrocarbonate. To determine the optimal pH and to determine the necessary amount of the precipitating agent, potentiometric titration of SSCN with a 10 % solution of sodium carbonate was carried out. The results of titration are presented in Fig. 1. To obtain nickel hydroxo salt, the solution of Na_2CO_3 was added drop by drop under permanent mixing to the spent electrolyte under pH control; the formed precipitates were separated by filtering, washed from water-soluble impurities, and dried at a temperature of 80–90 °C for 90 min. The dried precipitate was green, and its structure was loose. The obtained results are presented in Table 2.

According to the obtained data (see Fig. 1 and Table 2), the most complete precipitation of Ni^{2+} ions occurs at pH 10, which has formed the basis for the development of a technological flowchart of SSCN processing.

The composition of the obtained precipitate was studied by means of IRR spectroscopy (Fig. 2, curve *1*). At 650 cm^{-1}, a peak corresponding to the bending vibrations δ(Ni–O–H) is observed, which is characteristic of the α-form of nickel(II) hydroxide [13]. A broad peak at 1116 cm^{-1} is related to the stretching antisymmetrical vibrations of sulphate ions incorporated in the precipitate [14]. A doublet in the region of 1382–1474 cm^{-1} relates to the stretching vibrations of CO_3^{2-} group, its presence may be explained by the use of sodium carbonate as the precipitating agent [14]. Broad absorption bands within the wavenumber range 3400–3500 cm^{-1} relate to the stretching vibrations of OH-groups linked through hydrogen bonds, characteristic of the α-modification of $Ni(OH)_2$ [15]. So, as a result of precipitation from SSCN by sodium carbonate, nickel hydroxocarbonate was obtained. It contains nickel hydroxide in the α-form, which is characterized by a loose, unstable, fine structure.

The nature of processes taking place under heating of the obtained hydroxo salt was studied by thermal analysis. The TGA and DTA curves are presented in Fig. 3. The DTA data show that the mass loss curve (TGA) has three clearly pronounced peaks corresponding to evaporation of adsorbed (crystallization) water at a temperature

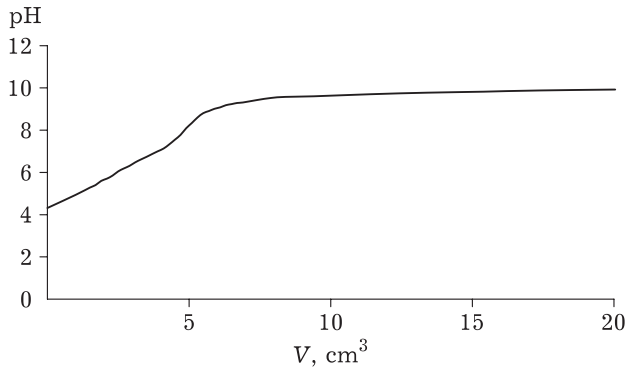

Fig. 1. The curve of potentiometric titration of nickel ions in the spent solutions from chemical nickel plating with sodium carbonate. *V* – precipitator volume.

of 60–100 °C, chemisorbed water at a temperature of 280±10 °C, and chemisorbed water at a temperature of ~420 °C, which agrees with the literature data [16]. It has been established [11] that a decrease in precipitate mass within the temperature range of 250–300 °C is caused not only by the removal of water but also by the loss of carbon dioxide, which accounts for 12 %. Calculations made on the basis of TGA data reveal that the ratio $Ni(CO_3)/Ni(OH)_2$ in the obtained precipitate is 0.056, that is, the major part of precipitated substance is nickel hydroxide. As a result of the thermal treatment of nickel hydroxocarbonate, black fine nickel oxide powder was obtained. It was analysed by means of IR spectroscopy. According to [11], the black colour of the oxide is due to the presence of excessive (above stoichiometry) oxygen in lattice points.

Clearly pronounced peaks are observed in the IR spectrum of nickel(II) oxide (see Fig. 2, curve *2*): at 1028 cm^{-1}, corresponding to the stretching vibrations of sulphate ions [14]; at 1427 cm^{-1}, providing evidence that the precipitate contains carbonate ions brought with the precipitant [14]; at 1617 and 3447 cm^{-1}, related to the bending and stretching vibrations of water admixtures are present in the formed nickel(II) hydroxide and oxide precipitates, which allows

TABLE 2

Recovery of Ni^{2+} ions from the spent solutions of chemical nickel plating depending on solution acidity (pH)

Parameter	pH		
	8	9	10
C_{res}*, g/dm^3	0.1665	0.1129	0.0895
Recovery degree, %	94.93	96.56	97.27

* The residual concentration of nickel(II) in the sample.

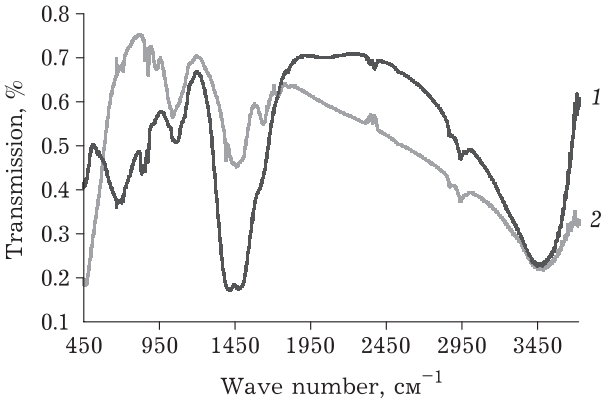

Fig. 2. IR spectra of nickel(II) hydroxide (*1*) and oxide (*2*).

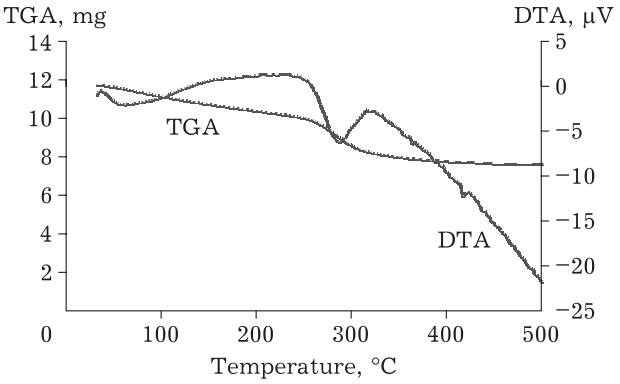

Fig. 3. The curves of thermal analysis of nickel(II) hydroxide.

using the precipitated substances for making the initial working solutions for chemical nickel plating (SCN).

The experiment carried out by us proved the possibility of two versions for SSCN regeneration. The first version involves nickel hydroxo salt. Nickel was precipitated by a 10 % solution of sodium carbonate at pH 10, followed by thorough washing of the obtained precipitate to remove water-soluble impurities, and drying at 80–90 °C. To improve the quality of regenerated electrolyte, and to decrease the consumption of sulphuric acid, nickel hydroxide was initially dissolved in sodium acetate [18], so that its amount corresponded to its content in SCN; the final dissolution of the precipitate was carried out in 5 % sulphuric acid. Other SCN components were introduced into the obtained solution under pH control within the range of 4.1–4.7.

The second version of SCN preparation involves the use of nickel oxide obtained from the precipitated nickel hydroxocarbonate, washed and dried preliminarily, with final drying in a muffle furnace at 500 °C for 90 min to the constant mass, and then the working electrolyte was prepared according to the scheme described above.

Chemical nickel plating solutions prepared according to both versions were used to deposit nickel coating on brass products. Metal samples were placed for 2 h in the prepared solutions under permanent mixing and heating at 90 °C.

The thickness of nickel coating, which was determined to be 12.54 μm, was successfully measured only in the case of the solution prepared from nickel hydroxide. In the second version, nickel coating is characterized by non-uniform friable structure, which makes it impossible to measure the thickness of the coating precisely. Its approximate value is several hundredths of a micrometer. So, a high-quality nickel coating may be obtained on a brass product using a SCN prepared using nickel hydroxide. Therefore, a more optimal and economically favourable version is the method to utilize SSCN to nickel hydroxocarbonate for obtaining initial SCN.

CONCLUSION

It has been determined by potentiometric titration that the most complete precipitation of nickel ions from SSCN by sodium carbonate occurs at pH 10. The composition of precipitated nickel hydhroxocarbonate was studied by IR spectroscopy and thermal analysis. The ratio $Ni(CO_3)/Ni(OH)_2$ was determined to be equal to 0.056, and precipitated nickel hydroxide is mainly in the α-form.

Two versions are proposed for the technological scheme of SSCN regeneration for obtaining SCN prepared from nickel(II) hydroxocarbonate and oxide. It has been determined by SEM that high-quality nickel coating is obtained using the electrolyte prepared on the basis of nickel hydroxocarbonate. The proposed version of SSCN recycling allows making the working electrolyte without using additional amounts of expensive nickel salt and at the same time reduces the negative environmental effect.

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