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NICKEL PIGMENTS PREPARATION BY SPENT NICKEL-PLATING ELECTROLYTE PRECIPITATION

A way to recycle spent waste sulfuric acid nickel electrolytes by nickel compounds extracting is offered and in this paper. The nickel (II) ions concentration was defined by chemical analysis and solid phase composition were determined by elemental analysis.

Slightly soluble nickel (II) compounds were precipitated with sodium hydroxide solution and saturated sodium orthophosphate solution during boiling. Also waste degreasing solution containing sodium hydroxide, sodium carbonate and sodium phosphate was used. Nickel (II) ions extraction degree for degreasing solution precipitation was 97%, and for sodium hydroxide solution or sodium orthophosphate solution precipitation – 99.9%. For nickel (II) compounds obtained X-ray analysis, elemental analysis and thermal analysis were carried out, their IR-absorption spectra micrographs were obtained. Colored compounds obtained from waste electrolytes had various shades of green colour scheme and high concentration of chromofore ions. That made them possible for pigments producing. The precipitates obtained were dried, calcinated, milled, sifted and then used as pigment compositions.

Key words: spent nickel electrolytes, pigment, nickel oxide, nickel phosphate, recycling.

Introduction. Currently there are over 140 industrial enterprises in Belarus having electroplating industry as part of it [1]. Electrocoatings are the way to protect metals against corrosion. They also provide increase in electroconductivity, lasting qualities and other properties of the product. Zinc, chrome and nickel coating are widespread in Belarus.

The main functions of nickel coating are protective and decorative. In addition nickel coating is widely used in chemical industry in order to protect equipment working area from different aggressive environments exposure. Nickel coating is used as interbedded sublayer before other coatings application on steel to provide rigid adherence of support coatings. It is used to lasting qualities increase of rubbing parts as well.

Modern nickel-plating electrolytes contain special nonorganic and organic additives that prevent sliming, increase anode solvability, increase coating hardness and decrease its interparticular porosity. This additives allow to get bright deposits with basic metal leveling directly from baths [2, 3].

Electroplating industry considerably increases environmental stress because of huge amount of wastewaters. Although present electrolytes are non-fluctuating and during the operation are subject to batch purification and composition correction but in course of time electrolytes are required to be replaced as a result of their pollution. At different enterprises discharging of spent electrolytes is carried out at different intervals (from several times a year to once in a five-year time) after accumulation in work solution irreversibly deteriorating technological parameters of plating bath operation.

Spent electrolyte solutions volume is not usually large and is estimated by the size of plating baths and their number at an enterprise. The plat-

ing baths volume normally vary from 0.5 to 1.5 m³. Nevertheless, spent electrolytes solutions are highly concentrated (main compounds content till 200–250 g/l) and considerably pollute environment.

Plating industry spent solutions have high concentration of chromophore ions. For this point it becomes reasonable to study the study possibility to obtain colored compounds from electrolytes solutions. These compounds can be used during for pigments producing and through this the research will help to partially solve the problem of import substitution of nonorganic pigments for industrial needs.

In this paper studies on obtaining of slow-soluble nickel compounds (II) from spent nickel-plating solutions have been carried out. As a result of the research, obtained nickel-containing compounds were used during the process of formation of pigment compositions.

Experimental technique. Nickel compounds were obtained by deposition method. To obtain nickel compounds (II) spent nickel-plating electrolytes, sodium hydroxide, sodium phosphate solutions, spent degreasing solution of the following content were used: NaOH – 6 g/l; Na₂CO₃ – 30 g/l; Na₃PO₄ – 30 g/l.

Ni²⁺ content in testing solutions was established beforehand by chemical analysis and composition of condensed phase – by elementary analysis.

Research of homogeneousness of samples and element-by-element distribution of certain elements in them was carried out with the help of scanning electron microscope JEOL JSM – 5610LV (Japan) with system of electron probe energodispersed XF-analyzer by JED 22-01.

X-ray diffraction patterns were used to study phase composition of the obtained samples and were recorded at on a D8 ADVANCE diffractome-

ter by Bruker (Germany) or DRON-3 diffractometer (USSR) using $\text{CuK}\alpha$ -radiation in the range of 2θ angles of $20\text{--}80^\circ$.

Infrared absorption spectra of samples were used for compounds identification and also for qualitative evaluation of free and associated water content in samples. The spectra were recorded into tableted with KBr ("c. p.") mixtures with the help of IR-Fourier spectrometer NEXUS by THERMO NICOLET within the interval of wavenumber of $350\text{--}4,000\text{ cm}^{-1}$. Sample weight was $\approx 1\text{ mg}$. Estimated faulty proportion of vibration frequency was less than $\pm 2\text{ cm}^{-1}$.

Main part. To establish quantitative and qualitative composition of spent nickel-plating electrolyte the solution was evaporated and then condensed phase was exposed to elementary analysis, the results of which are provided in Table 1.

Table 1

Results of elementary analysis of evaporated spent nickel-plating electrolyte sample

Chemical element	Wt %
O	31.47
Si	0.42
S	11.96
Cl	8.11
Ni	48.04
<i>Total</i>	100.00

Provided data testify about presence of nickel, sulfur, chlorine, silicon and oxygen in the sample. According to the data [2], nickel sulfate and nickel chloride (II) are the main component of acid nickel-plating electrolyte that corresponds to the obtained results of elementary analysis.

Nickel hydroxide (II) was obtained from spent nickel-plating solution by sodium hydroxide deposition ($\text{NaOH} - 30\text{ g/l}$).

Hydrated nickelous phosphate was obtained by nickel ions deposition (II) saturated at the temperature of 25°C by solution of Na_3PO_4 . Deposition was carried out during the boiling.

While using degreasing solution to obtain nickel-containing compounds residue necessary quantity of precipitator [4] was determined beforehand. The maximal ion recovery degree is Ni^{2+} , consequently, maximal output of end product took place at double excess of precipitating degreasing solution to the initial number of Ni^{2+} .

Initial and residual Ni^{2+} ion concentration was determined by direct Ni^{2+} ion titration by EDTA solution with murexide. Each solution was exposed to titration of 5 samples, obtained data were averaged. In accordance with the results of titration Ni^{2+} mass in analyzing samples was calculated.

Initial concentration of Ni^{2+} in spent nickel-plating electrolyte was 68.10 g/l . Residual nickel

ion concentration in precipitation filtrate was 1.80 g/l for degreasing solution and 0.06 g/l for sodium hydroxide solution.

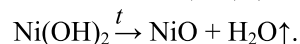
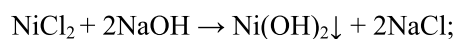
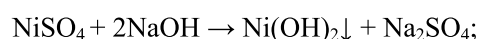
Nickel ion recovery rate was calculated in accordance with formula:

$$\frac{C_{\text{init}} - C_{\text{resid}}}{C_{\text{init}}} \cdot 100\%,$$

where C_{init} и C_{resid} – initial and residual nickel ion concentration (II) in a sample.

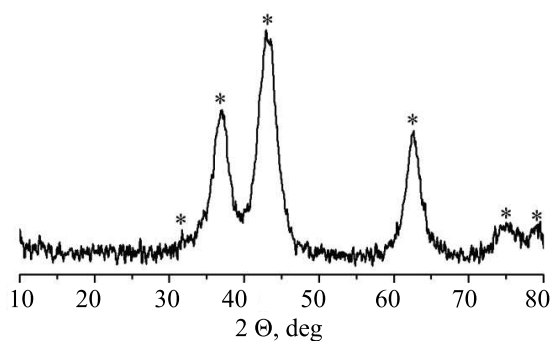
Calculated Ni^{2+} recovery rate while using of degreasing solution and NaOH solution was 97 and 99.9% correspondently.

Nickel oxide (II) from spent electrolyte was obtained with the help of the following reactions:



Nickel hydroxide (II) was precipitated by concentrated solution of sodium hydroxide ($\text{NaOH} - 30\text{ g/l}$), with 10% excess to Ni^{2+} content in solution. Precipitation was carried out at room temperature and constant mixing. Residue was exposed to five-time decantation followed by filter washing. Dried residue was thick, finely-divided and dark green. According to the data [5], nickel hydroxide (II) dissolved into nickel oxide (II) and water at the temperature of 230°C , thus, filtered residue was dried, grinded in porcelain jar and then dehydrated in drier at the temperature of 240°C during two hours. While dehydrating color of residue was changed that goes in conformity with reference data, according to which color of NiO depending on the method of obtaining and content of water in a sample is varied from light to dark green [5]. Dehydrated sample was grinded in agate mortar and was sifted through the sieve with hole size of 0.2 mm .

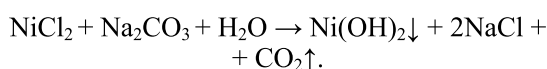
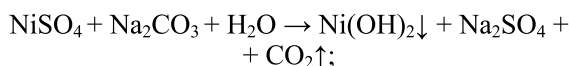
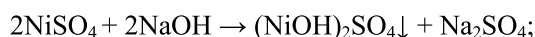
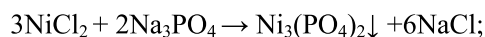
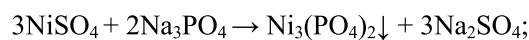
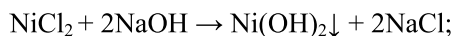
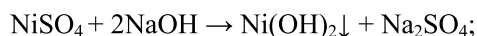
Obtained sample had grey-green color. It was one-phased according to XRD and appeared to be NiO oxide (Fig. 1).



* NiO phase (JCPDS ICDD No. 01-089-5881)

Fig. 1. X-ray diffraction pattern of nickel oxide sample

As degreasing solution contains sodium hydroxide, carbonate and phosphate, the residue can be the mixture of $\text{Ni}_3(\text{PO}_4)_2$ phosphate, $\text{Ni}(\text{OH})_2$ hydroxide, phosphates, sulfates and, possibly, some other nickel compounds. Slightly soluble nickel compounds can be formed after following reactions:



Precipitation was carried out at room temperature and stirring. Residue was filtered, washed and dried.

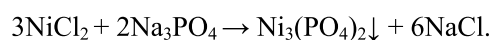
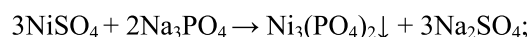
Results of elementary analysis of residue obtained from spent nickel-plating electrolyte by ion precipitation Ni^{2+} with degreasing solution are provided in Table 2 according to which tested sample consists of some amount of sulfur. Presence of sulfur compounds in residue can be explained by the forming of slightly soluble $(\text{NiOH})_2\text{SO}_4$ salt. Presence of a considerable number of sodium in residue compounds is difficult to understand and special study of condensed phase is required.

Table 2

Results of elementary analysis of residue sample obtained from nickel-plating electrolyte after precipitation with degreasing solution

Chemical element	Wt %
O	27.05
Na	6.41
Si	0.10
P	2.25
S	3.51
Ni	60.68
<i>Total</i>	100.00

While obtaining nickel phosphate (II) excess amount of saturated at the temperature of 25°C phosphate solution Na_3PO_4 was added to spent electrolyte. Obtaining of nickel phosphate (II) was carried out in accordance with the following reactions:



Precipitation was carried out while boiling. After cooling residue of crystalhydrate $\text{Ni}_3(\text{PO}_4)_2 \times$

$\times 8\text{H}_2\text{O}$ [5] falls out from the solution. Residue was washed several times, filtered, dried to the firm condition, then reduced to a small size. Nickel phosphate (II) used in anticorrosion pigments has to correspond to certain requirements, in particular, mass fraction of water in it has to be minimal [4, 6].

The residue consisting of hydrated nickel phosphate was calcinated in muffle oven at the temperature of 860°C to get out of water. According to thermogram while heating of sample weight from 25 to 990°C mass loss is 42.9%, besides 42.5% of the mass is lost at the temperature of less than 860°C. Consequently, calcination at the temperature of 860°C results to almost complete removal of water from the sample.

Fig. 2 demonstrates IR-specter of sample 1 consisting of nickel phosphate crystalhydrate (II) (curve 1), and sample 2 calcinated at the temperature of 860°C within 1 hour (curve 2). IR-specter of sample 1 corresponds to $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ [7]. 3,441, 3,148, 3,010 cm^{-1} bands correspond to valence vibration of water molecules. Band shift into low-frequency region testifies of the fact that water molecules participate in formation of rather strong hydrogen bonding. In sample 2 specter decrease of these bands intensity is observed and obtained specter corresponds to specter $\text{Ni}_3(\text{PO}_4)_2$ [7]. The presence of 1,595 cm^{-1} band, associated with bending vibration of water molecules, in specter of sample 2 can be explained by absorption of some amount of atmospheric moisture by water-absorbing sample of nickel phosphate after calcination.

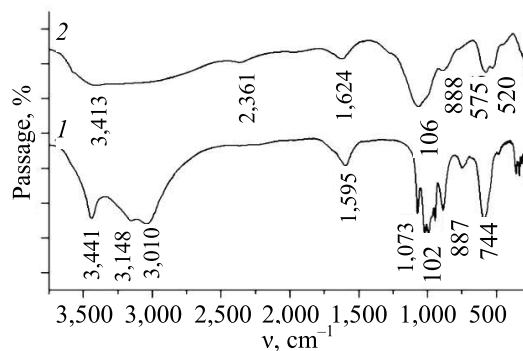


Fig. 2. IR-absorption spectra:
1 – sample 1; 2 – sample 2

After calcination the sample was grinded in agate mortar and sifted. The color of the sample was dark-green.

Obtained nickel compounds were characterized by even color of different shade of green color that is connected with the content of special additives in spent nickel-plating solutions and different conditions of thermal processing.

Nickel oxide and nickel phosphate obtained from spent nickel-plating solutions were used for

pigment compositions. Chromophore Ni^{2+} ions are responsible for green color of pigments. For pigment compositions oil-absorption of the first and second type, acidity, water solubility and covering power were determined.

Conclusion. In this paper possibility of obtaining of coloured compounds, which can further be used in production of inorganic pigments from the wastes of industrial electroplating, has been studied. It was revealed that Ni^{2+} ions recovery degree from spent

nickel-plating electrolyte solutions while using of degreasing solution as precipitator was 97% and while using of sodium hydroxide or sodium phosphate solution – 99.9%. Obtained nickel compounds (II) can be used for obtaining of anticorrosion pigments. High spent solutions purification degree from Ni^{2+} ions was achieved. Using of recommended techniques and reagents allows to decrease the negative environmental impact of nickel compounds.

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