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THE TECHNOLOGY OF OBTAINING COMPLEX ANTICORROSIVE PIGMENTS FROM ZINC-CONTAINING WASTE WATER

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Abstract. The technique for environmental protection from heavy metals is proposed in this paper. The objective of this research is development of utilization technology of metal-containing hazardous sewage with the reception of anticorrosive pigments. Zinc containing model solutions and waste water were used for this study. Cobalt was used as a cation chromophore. The method of potentiometric titration has been applied for research of precipitation process. X-ray phase analysis, electron microscopy, derivatograph method, power dispersion spectrometry, and spectrophotometric methods were used to learn the pigment properties.

Keywords: anticorrosive pigments, waste water, technology.

1. Introduction

Growing anthropogenous load on environment threatens health of the present and future generations. In this connection the problems of working out and introduction of low-waste technologies, processes of recycling of sewage and toxic waste, as well as obtaining and use of ecologically safer products come to the fore [1-2].

The basic sources of pollution and contamination of reservoirs are insufficiently cleared sewage of industrial and municipal enterprises, large cattle-breeding complexes, wastes of ore minerals production, waters of mines, dump waters of water and railway transport, *etc*. Polluting substances, getting to natural reservoirs, lead to qualitative changes of water (occurrence of unpleasant smell, smack, *etc*.), as well as to changes in chemical compound of water, occurrence of floating substances on water surface and their deposition at the bottom of reservoirs.

The most harmful action on environment and human body is rendered by heavy metals. Scientific researches show that a considerable quantity of heavy metals, such as copper, lead, zinc, nickel, and cobalt can appear in water owing to ingress of industrial wastes into the hydrosphere. Heavy metals are powerful stimulators and activators of cancer and cardiovascular diseases. They tend to accumulation in food chains, which increases their hazard to human health. Pollution by heavy metals occurs in the entire biosphere. All known ways of heavy metals removal from water are very expensive or, which is even worse, involve use the substances which are toxic themselves [3].

At the same time, because of strengthening of atmosphere aggressiveness effective protection of metals against corrosion is necessary and the need for active anticorrosive pigments, which possess sufficient passivating action, grows [4-5]. Because of the rise in price of anticorrosive pigments from pure materials as well as in view of natural resources exhaustion problem, production of pigments from sewage and waste is promising both from economic and ecological standpoints.

In the given work the technology allowing not only to lower anthropogenous load on natural environment, but also to receive a product able to replace toxic chrome-containing anticorrosive pigments is offered.

2. Experimental

For this research we used modeling solutions and sewage which incorporate zinc cations. As a cation of the chromophore we used cobalt. Sedimentation of cations of zinc from sulfate solution was performed by 0.15N sodium phosphate. Double-cobalt and zinc orthophosphate were precipitated from solutions of zinc sulfate (II) and cobalt (II). Parity of cobalt cations to zinc cations was changed as follows: 0:1, 1:1, 3:1, 1:3. Investigation of the process was carried out using the method of potentiometric titration to a pH meter. As the measuring electrode, the glass electrode of ESL-106 03/7 grade was used, silver chloride of TDL-1000 grade served as the reference electrode. The temperature of the studies was 298 K, powders burning temperature was 1073 K.

Trace concentrations of cobalt and zinc were determined by titrimetric known techniques [6]. Properties of the pigment were studied by X-ray diffraction, electron microscopy, and energy dispersive spectrometry. Optical characteristics were studied by the color comparator. Radiographs were obtained on DRON-2.0 powder with K_{Co} radiation.

3. Results and Discussion

When adding sodium phosphate to zinc-containing wastewater precipitate of zinc phosphate $Zn_3(PO_4)_2$ or $Zn_3(PO_4)_2 \cdot nH2O$ is formed, which is used as white pigment. Zinc phosphates are one of the most common anti-corrosive pigments, designed for water- and organo-soluble varnish-and-paint materials. However, it is interesting to study the effect of cobalt on the change of properties of the produced powder.

The research results of the system of $ZnSO_4$-Na_3PO_4 and $ZnSO_4$-oSO_4-Na_3PO_4 by potentiometric method are presented in Figs. 1 and 2.

The reaction of zinc sulfate $ZnSO_4$ with sodium phosphate Na_3PO_4 results in formation of neutral salt – zinc phosphate $Zn_3(PO_4)_2$. The salt formation occurs by the reaction:

$$2Na_3PO_4 + 3ZnSO_4 \rightarrow 3Na_2SO_4 + Zn_3(PO_4)_2\downarrow \quad (1)$$

Besides the following reactions are possible:

$$Zn_3(PO_4)_2 \rightarrow 3Zn^{2+} + 2PO_4^{3-} \quad (2)$$

$$Zn^{2+} + H_2O \rightarrow ZnOH^{+} + H^{+} \quad (3)$$

$$Zn^{2+} + 2H_2O \rightarrow Zn(OH)_2 + 2H^{+} \quad (4)$$

$$PO_4^{3-} + H^{+} = HPO_4^{-} \quad (5)$$

In the presence of cobalt cations occurrence of similar reactions as well as formation of intermediate complex salts of cobalt and zinc can be assumed.

As seen from zinc phosphate solution pH dependence on the volume of sodium phosphate (Fig. 1) the addition of the first portions of Na_3PO_4 decreases pH, which is associated with the zinc salts hydrolysis. Next, we observe a jump of pH values corresponding to the formation of basic zinc phosphate and then medium zinc phosphate. The curves at different content of cobalt are similar by their nature. However, as seen in Fig. 2 the increase of cobalt content changes pH of phosphate formation and a smoother shape of the curve corresponds to the formation of several intermediate compounds.

The formation of double orthophosphate of cobalt and zinc can be shown schematically by the following reaction:

$$3nZnSO_4 + 3mCoSO_4 + 2(m+n)Na_3PO_4 \rightarrow$$
$$\rightarrow nZn_3(PO_4)_2 \cdot mCo_3(PO_4)_2 + 3(m+n)Na_2SO_4 \quad (6)$$

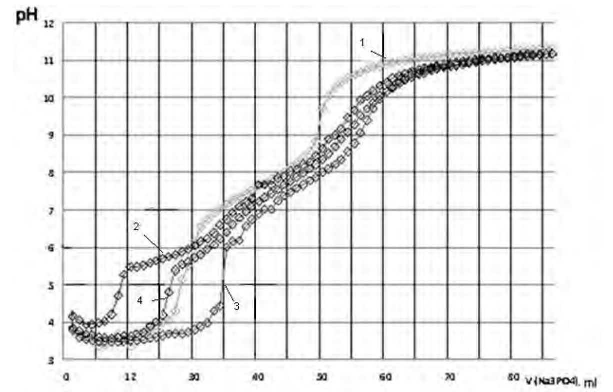


Fig. 1. Dependence of solution pH on the sodium phosphate volume in $ZnSO_4$-$CoSO_4$-Na_3PO_4. Zn: Co ratio: 1:0 (1); 1:3 (2); 3:1 (3) and 1:1 (4)

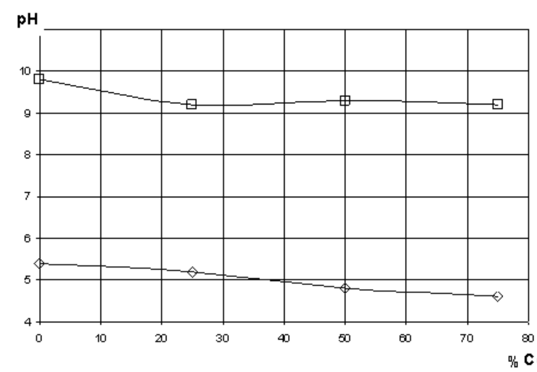


Fig. 2. Dependence of pH of cobalt phosphate formation on the cobalt content in $ZnSO_4$-$CoSO_4$-Na_3PO_4: basic phosphate formation (1) and medium phosphate formation (2)

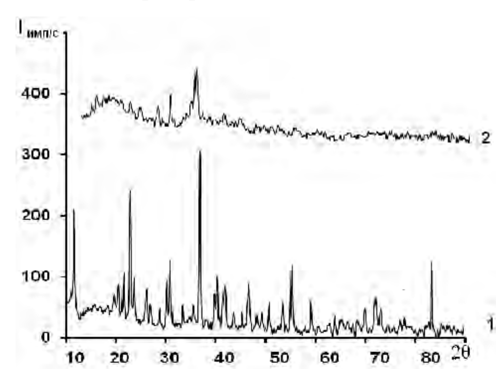


Fig. 3. X-ray diffraction of cobalt and zinc orthophosphate powders with $ZnSO_4$:$CoSO_4$ = 3:1: before burning (1) and after burning (2)

To establish the phase content of the resulting powders of double cobalt and zinc orthophosphates they were examined after pre-filtering and drying.

Fig. 3 shows the X-ray diffraction patterns of pigment of double cobalt and zinc orthophosphate before and after burning. It was found that the deposition of the compound formed $Zn_{2.5}Co_{0.5}(PO_4)_2{\cdot}2H_2O$, and after ignition, the system becomes biphasic. For the confirmation of this hypothesis microscopic and elemental analysis were conducted (Figs. 4 and 5).

In micrographs (Fig. 4) the presence of two phases is seen: depleted with cobalt (1) and enriched with cobalt (2).

Then the color characteristics of the obtained powders were investigated (Table 1).

The results of the comparative tests of double orthophosphate powders of cobalt and zinc, namely, the change of their color before and after burning are presented in Table 1 and Fig. 6.

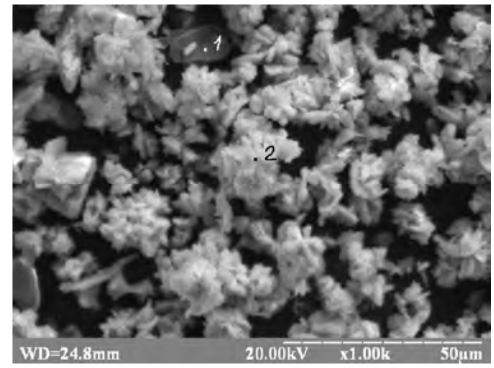


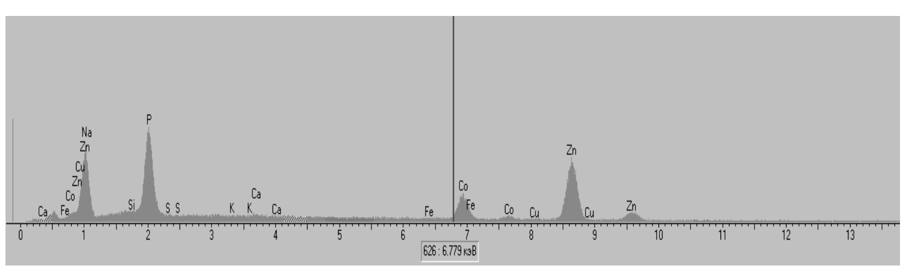
Fig. 4. Photomicrograph of double cobalt and zinc orthophosphate powder

Table 1

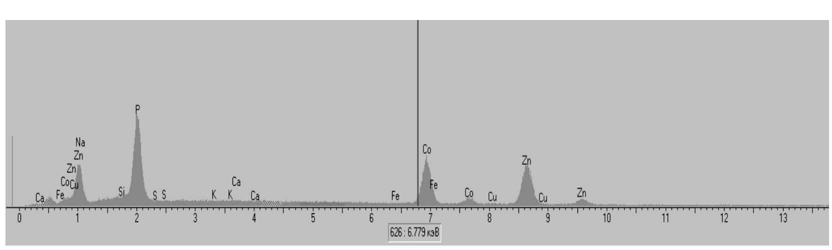
Color characteristic of $ZnSO_4$ - $CoSO_4$–Na_3PO_4 pigments before burning

Zn:Co ratio	*CSR*, %	*X*	*Y*	*Z*	*x*	*y*	*λ*, nm	*P*, %
1:1	45.53 44.94	54.71	42.61	20.05	0.4660	0.3630	2.9	519
1:3	45.95 45.22	54.11	42.12	19.68	0.4667	0.3634	3	516
3:1	45.39 45.90	54.10	42.22	19.81	0.4658	0.3634	3	519

Notes: *X*, *Y* and *Z* – coordinates of color; *x* and *y* – coordinates of chroma; *SRC* – specular reflection coefficient, %; *λ* – wave length, nm; *P* – color purity,%.



a)



b)

Fig. 5. Composition of the cobalt and zinc orthophosphate powders: of the second hase $Zn_{3-x}Co_x(PO_4)_2{\cdot}H_2O$ (a) and of the first phase - $Zn_{2,5-x}Co_x(PO_4)_2{\cdot}$ $2H_2O$ (b)

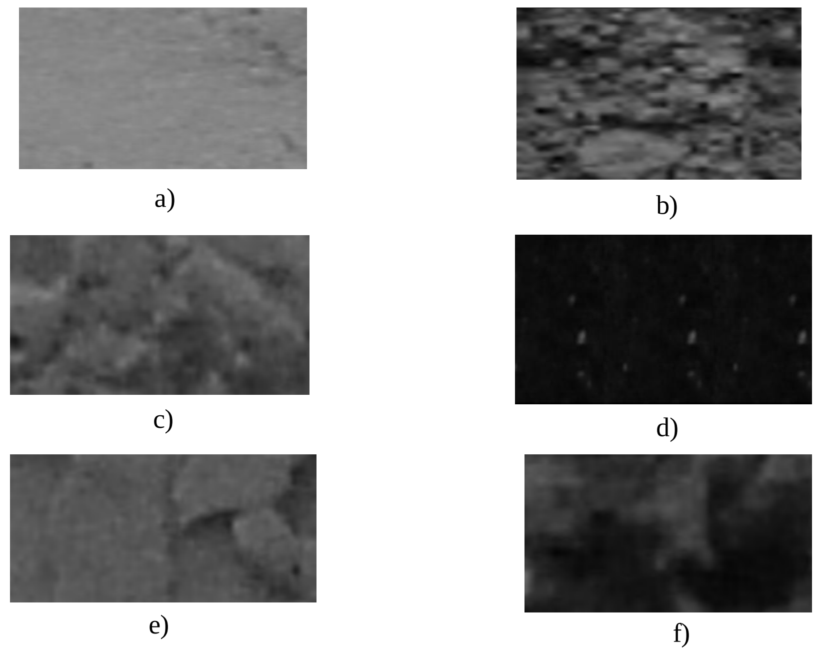


Fig. 6. Photos of double orthophosphate of cobalt and zinc powder at different ratio of $ZnSO_4$-$CoSO_4$ before burning (a, c, e) and after burning (b, d, f): $ZnSO_4$:$CoSO_4$ = 3:1 (a, b), 1:3 (c, d) and 1:1 (e, f)

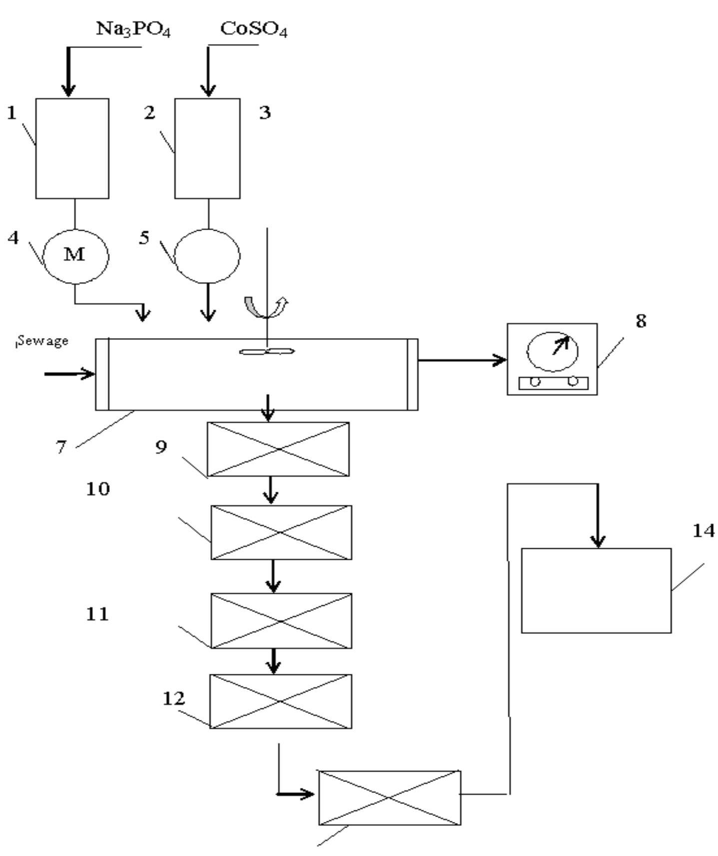


Fig. 7. The schematic technological scheme of wastewater treatment

The experiments allowed to develop the technological scheme of zinc-containing waste water cleaning. Schematic diagram of the process is shown in Fig. 7.

The required number of Na_3PO4 is fed under stirring from the tank 1 through the measurer 4 to the reactor 7 (Fig. 7), and $CoSO_4$ solution is fed to the reactor 7 from the tanks 2 through the measurers 5. Sewage was fed to the reactor 7 beforehand. The temperature in the reactor is kept at about 293±2 K. During the agitation in the tank pH of the solution is determined with pH-meter 8, which should have the value of 12. Precipitation of the double orthophosphate of cobalt and zinc is carried out at constant pH. On reaching pH = 7–8 suspension enters the thickener 9, filter 10 and then passes into the dryer 11, which dries the powder at the temperature of 363–373 K. Then the dried powder gets into the furnace 12, where it is roasted. Then it is milled in disintegrator 13. The powder obtained contains microparticles of 0.5–0.6 microns with high quality, which is achieved by improving the dispersion of pigment, reduction of structural viscosity and stability of the suspension. At the end of the process the device is cooled to room temperature, after which the final powder of double cobalt and zinc orthophosphate unloaded from the apparatus. Time of the deposition process is 0.5–1 h.

4. Conclusions

Investigation of the deposition process of zinc phosphate and complex zinc and cobalt phosphates was carried out. Conditions for obtaining double phosphate of cobalt and zinc were established. The color characteristics of pigments and their relation to phase composition were determined. Based on these studies the technological scheme of zinc-containing wastewater purification can be offered. To vary the color of the pigment from pale pink to violet it is suggested to change the amount of cobalt cations and the burning temperature.

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ТЕХНОЛОГІЯ ОДЕРЖАННЯ СКЛАДНИХ АНТИКОРОЗІЙНИХ ПІГМЕНТІВ ІЗ ЦИНКВМІЩУЮЧИХ СТІЧНИХ ВОД

Анотація. *Запропоновано метод захисту довкілля від важких металів. Об'єктом дослідження є технологія очищення стічних вод з одержанням антикорозійних пігментів. Як хромофор використано катіон кобальту. Методом потенціометричного титрування досліджено процес осадження. Властивості одержаного пігменту вивчено за допомогою рентгенофазового аналізу, електронної мікроскопії, енергодисперсійної спектрометрії, спектрофотометрії.*

Ключові слова: *антикорозійні пігменти, стічні води, технологія.*