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Synthesis and Study of Inorganic Pigment Properties on the Basis of Dead Chrome Catalyst.

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ABSTRACT

Generation of unprocessed wastes of industrial production is the key part of multi-factor negative impact on environment. The technologies of catching and neutralization of discharges and wastes have been developed extremely slow, as a result of it, the level of utilization remains to be low (only half of them is reused in production). All these concern in full measure chemical industry and adjacent branches of production – coal industry, mining, metallurgy, energy. In particular, only in chemical industry it has been calculated about 800 names of wastes. Major part of wastes is deleterious and hazardous to biosphere, processing toxicity, chemical, biological activities, corrosiveness, inflammability and explosibility. On the other hand – industrial wastes contain valuable elements, in particular different metals, the reserves of them are exhaustible. Waste burial is unpractical from the point of view of stability of functioning of industrial complex on the whole. The industrial wastes are often multi-component mixtures of substances of heterogeneous chemical composition, having different physical and chemical properties. The processes of interaction between the components and the background objects and by-product assimilation bring a considerable uncertainty in chemical composition and material constitution of industrial wastes. The technologies of waste recycling to receive the products, specifically inorganic pigments, involve the complex of methods of processing with the use of different modifiers to obtain the needed complex of physical and chemical properties defining the functional characteristics of the target product.

Keywords: dead catalyst, pigment, synthesis, ceramic processing.

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INTRODUCTION

Reprocessing in order to derive pigments and loading agents of various wastes of chemical industry and adjacent branches of production is an actual research guideline.

Thus, for example, calcium ferrites, derived from pure iron oxide and calcium oxide, applying ceramic processing, are characterized by high anticorroding properties and widely used in paint and varnish industry [1-2].

Substantial are the volumes of industrial iron-containing waste which offers ample opportunities of deriving ferrite pigments. The most hazardous industrial wastes are waste waters discharged from galvanizing plants. Their composition includes compounds of metals that have delirious impact on ecosystem. They take part at all stages of hydrologic cycle, passing into solution or forming colloidal systems [3].

Search for methods of gaining highly efficient pigments in order to use them in the corrosion-inhibiting primer base from industrial wastes is exceedingly topical [4-6]. More attention is paid to ecological compatibility of the materials and availability of raw materials.

Advanced line of research is determination of conditions of synthesis, choice and preparation of source materials and modifying agents in order to gain inhibiting pigments for anticorroding composition [7-8].

RESEARCH METHODOLOGY

The object of research is the samples of dead chrome-containing catalyst. The methods of researching inhibiting properties.

The methods of aqueous extraction of pigment: 15 g of pigment was placed into 150-300ml glass, 50ml of distilled water was poured and brought to the boil and kept boiling for 30 minutes. The suspension was cooled, filtered, filled in volumetric flask and brought the volume to 50 ml of distilled water.

Determination of the current of corrosion

The current of corrosion was determined from Stern Giri equation by means of fitting Tafel constant and polarization resistance, that fit the best convergence of experimental polarized data with theoretical curve. The equation connects the current of corrosion, polarized corrosion and Tafel constant in the field of mixed kinetics (that is, when neither cathodic, nor anodic reaction can be neglected):

$$\mathrm{I} = \frac{b_a \cdot b_c}{2{,}303 \cdot (b_a + b_c) \cdot R_p} \cdot \left[\exp \cdot \left(\frac{2{,}3 \cdot \Delta E}{b_a} \right) - \exp \left(- \frac{2{,}3 \cdot \Delta E}{b_c} \right) \right],$$

where I – current, measured by polarization;

ΔE - polarization (shift of sample potential in relation to corrosion potential).

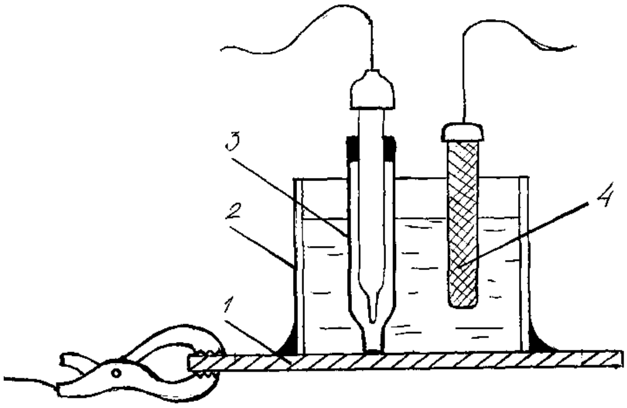
ba, bc – Tafel constants;

Rp – polarized resistance is evaluated by tangent of the slope of polarization curve at a point on stationary potential.

$$\frac{b_a \cdot b_c}{2{,}303 \cdot (b_a + b_c) \cdot R_p} = I_{кор},$$

i.e., the first factor of right side of equation is equal to required current of corrosion.

It was used three electrode electrochemical cell (figure 1). The latter was prepared by gluing of hollow glass cylinder with bore diameter of 3 sm onto the steel sample. The main electrodes were the section of steel of 08 kp (with an area of 7.07 sm^2), forming the bottom of glass, and auxiliary carbon electrode. 20ml of the studied electrolyte – water extract of the pigment, was poured into the formed cell. In order to provide the needed electroconductivity the electrolyte was prepared on the basis of background salt solution (NaCl).



1 – steel plate; 2 – glass cylinder; 3 – silver-chlorine electrode; 4 – auxiliary electrode

Figure 1: Electrochemical cell

If the current of corrosion in aqueous extract is less than in background electrolyte then the pigment exhibits inhibiting properties. The greater this difference is, the greater inhibiting efficiency of the pigment is.

The method of linear polarization defined by F. Mansfeld (Rockville International Center on Corrosion, the USSR) was assumed as a basis.

The samples became ones with glued glass cylinders into which electrolyte was poured, placed into Faraday cage and connected to the terminal of potentiostat. Contact surface with electrolyte was 7.07 sm^2.

Thermal analysis of samples of dead catalysts and modified products was performed using the device NETZSCH STA 499F3. Firing temperature interval was specified over the range of temperatures 30 and 1000°C with heating step 10 degrees per minute. Such conditions are the most reasonable to obtain qualitative result. Before firing the samples were reduced to powder for the purpose of volume gain of specific surface.

X-ray structure analysis

Registration of diffraction spectra was conducted using powder diffractometer Shimadzy XRD-7000S, on CuKα radiation with long wave α=1.54060 nm, with using nickel monochromator on diffracted beam, step 0.0008A_1 and unit exposition at point - 3 sec; and D2 PHaserBruker on CuKα radiation with long wave α=1.54060 nm.

Diffraction spectra processing and existing crystalline phases diagnostics is conducted by means of original interactive computer system EVA, version 4.0, designed for the study of mineral substances.

THE RESULTS OF RESEARCH AND DISCUSSION

Chromate crowns containing anion CrO_4^{-2} capable of passivating metal surface refer to the most widespread effective anticorroding pigments [9-10].

In spite of toxicity, chromate pigments keep to be applied, the alternative has not been found so far. Besides, chromate pigments differ by high cost conditioned by limited source of raw materials of their production. One of the possible ways of its replenishing is the use of chrome-containing anthropogenic wastes, the hypertoxicity of which causes considerable problems of with their burial. In this connection, the researches aimed at search for optimal solution in development of anticorroding pigments are the most urgently needed.

At the first stage of the work in consideration of mineral composition the possibility of using directly analyzed wastes was examined: furnace waste from electrostatic precipitator (FW) and equilibrium catalyst waste (CW) as pigment filling compound.

The obtained data on painting-technical parameters of FW, CW and red ferrioxide pigment (RFP), presented in table 1, allows to make preliminary conclusion about possibility of using wastes to be included in paints and varnishes.

Table 1 Painting-Technical Parameters

	Oil absorption , g/100g	Density, g/sm^3	The content of water-soluble substances, %	pH of water extract
Red ferrioxide pigment	25	7.72	0.2	7.0
FW	30-33	3.20	1.48	7.13
CW	32-38	3.29	1.13	7.43

The important parameters of pigments as the components paint and varnish systems are oil absorption and density, depending on specific surface, wetting ability and chemical composition. Knowledge of these indices is also needed for writing formula of paint and varnish materials.

To compare, oil absorption of zinc tetraoxichromate (ZTOC) widely used in corrosion-inhibiting prime coating equals 32 g/100 g, density – 3.50 g/sm^3.

Not high values of oil absorption of the first kind of the analyzed products allow to make conclusion about possibility of achieving high level of coating.

Partial aqueous solubility is needed for pigments intended for using in corrosion-resistant coating, just aqueous-soluble components, possessing the property to inhibit corrosion processes on the surfaces of metals, are their active principle. Depending on chemical composition the soluble compounds passing into aqueous phase can both inhibit the development of corrosion process and accelerate it. In any case the content of water-soluble substances must be optimal: sufficient to gain the required concentration of inhibitor compounds of corrosion and low in order not to cause the rapid corrosion of pigment and reduction of resistant properties of coating. The compounds of chrome 6 + contained in the wastes can provide corrosion-inhibiting ability in the composition of protective coating.

Corrosion-preventive actions of pigments were specified in consideration of characteristics of aqueous extracts being in contact with steel surface. Aqueous extracts of the studied wastes have neutral reaction. Corrosive potential of steel being in contact with extracts was established in the area of passive state of surface (figure 2).

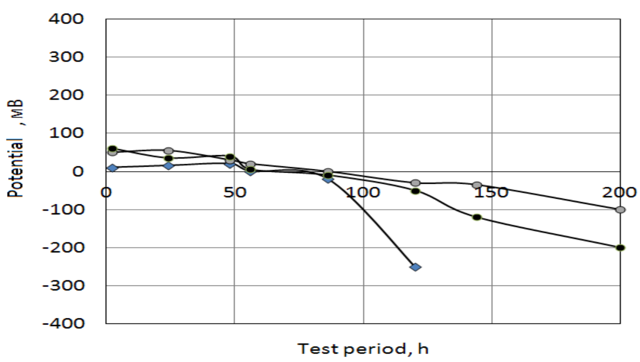


Figure 2: Kinetics of corrosive potential of aqueous extracts
RFP (1); EW (2); CW (3)

For the purpose of increasing reliability of results the inhibiting ability of the studied objects in aqueous medium in the presence of a corrosion active agent (in aqueous extracts in 3% solution NaCl) was additionally estimated by the method of low linear polarization using potentiostat IPC-Pro, controlled by computer. Polarization curves on steel samples in contact with aqueous extracts were taken in three electrode cell in the range of polarization ±30 mV at the speed of potential sweep 0,2 mB/s. Widely used inhibiting zink pigmenttetraoxichromate (ZTOC) exhibit high inhibiting properties only in coatings, and its aqueous extract in neutral mediums does not have passivating effect on steel.

The examples of conducting electrochemical experiments of aqueous extracts of source wastes are illustrated in figure 3.

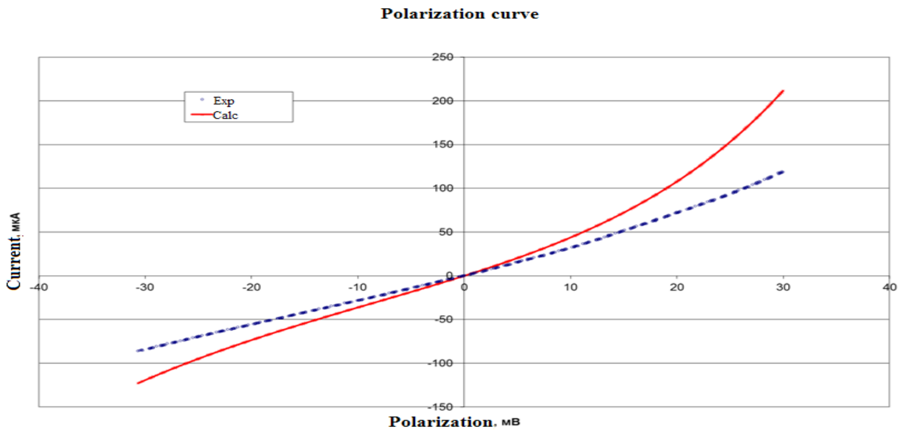


Figure 3: Potentiodynamic polarization curves, characterizing steel behavior 08 kp in contact with extract of CW

The principal qualitative criterion may be the current if corrosion of steel $I_к$ (mA/sm^2). Data in figures 4-5 and so forth are the results of statistic manipulation of polarization curves taken on five parallel samples.

Amount of current of corrosion in the background electrolyte was 20 mA/sm^2, in extracts FW - 13 mA/sm^2, ОК - 7 mA/sm^2.

For the purpose of optimization of content of water-soluble substances and increase in stopping power at the next stage it was studied the effect of thermal processing on the composition and properties of the analyzed wastes. To determine the temperature intervals of procedure of chemical reactions providing stabilization of the indicated parameters it was conducted thermoanalysis of the waste samples using the device NETZSCH STA 499F3. The firing temperature interval in the temperature range 30 and 1000°C with heating step 10 degrees per minute.

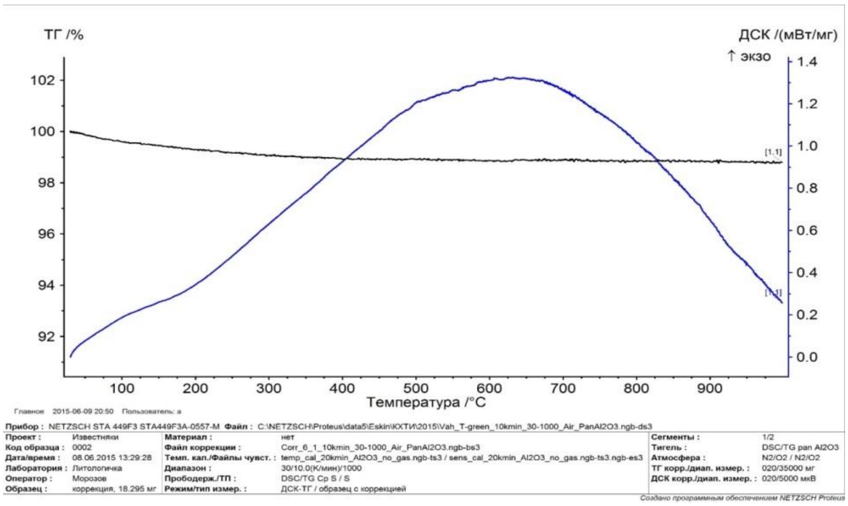


Figure 4: The results of thermoanalysis of FW. 1 – the curve of differential thermoanalysis, 2 – the curve of thermogravimetry,

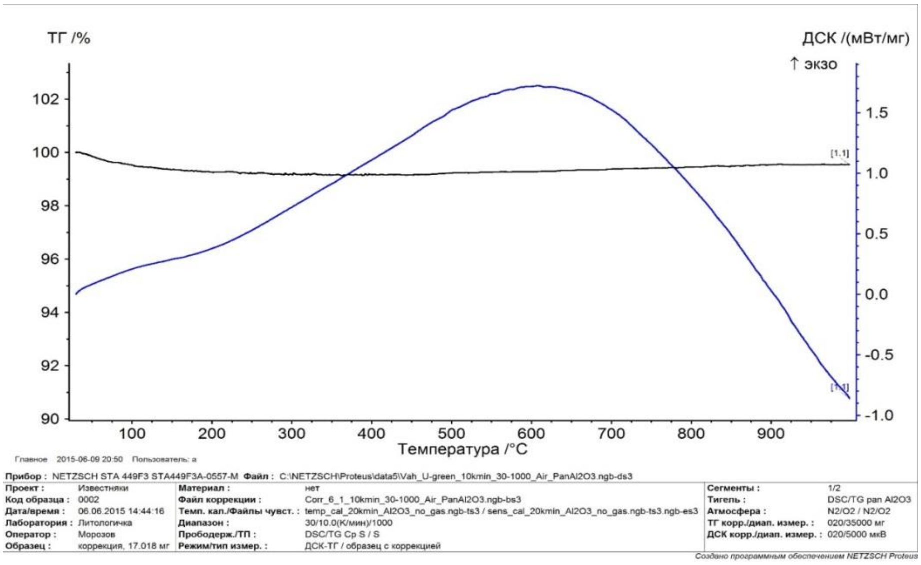


Figure 5: The results of thermoanalysis of CW. 1 – the curve of differential thermoanalysis, 2 – the curve of thermogravimetry.

Insignificant mass loss is connected with adsorption water extraction. Differential curves of thermal analysis (DTA) and differential thermogravimetry (ДTG) of the samples are characterized by the presence of one endothermic and one exothermal effects (figures 6-7).

The first eroded endothermic effect, observed in the temperature range 100-200°C, refers to adsorption water extraction, the next bright one at the temperature of 600°C for FW and 650°C for CW, to formation of potassium chromate according to reaction:

$$Cr_2O_3+K_2O \rightarrow KCrO_4$$

Estimation of physicochemical characteristics of the obtained products is demonstrated in table 2.

Table 2: Paint and-engineering parameters of the products of thermal treatment (3 hours of thermal treatment)

	Oil absorption, g/100g	Density, g/sm^3	The content of water-soluble substances, %	pH of water extract
FW 800°C	28,8	3.23	1.99	6.35
CW 800°C	38.6	3.34	1.91	7.25

Formation of potassium chromate led to insignificant increase of water-soluble substance content and decrease of pH in water extract.

Amount of current of corrosion in the background electrolyte was 20 mA/sm^2, in extracts of FW – 5.7 mA/sm^2, CW - 6 mA/sm^2. Thermotreatment led to insignificant increase of inhibitory action of water extracts. At the same time the content of water-soluble substances increased and the value of pH decreased. It can have negative effect on the properties of protective coating containing such pigments.

To increase inhibitory action it was conducted the modification by means of using combined thermotreatment of waste mixture with zinc oxide, interaction with which, as a result of high-temperature synthesis can provide the production of zinc chromate according to the reaction:

$$Cr_2O_3+ZnO \rightarrow ZnCr_2O_4$$

Zinc chromate is an active principle of high-performance corrosion-inhibiting pigment ZTOC to be widely used before.

The results of thermal analysis of charges containing different quantity of modifiers (figures 6-7).

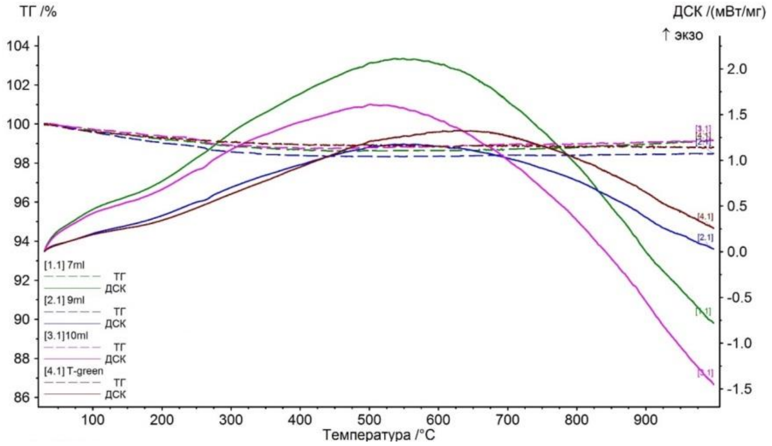


Figure 6: The results of thermoanalysis of mixtures of FW and zinc oxide. The curves of differential thermal analysis: 1.1 – 3%; 2.1 – 9%; 3,1 – 12%. 4.1 – source FW.

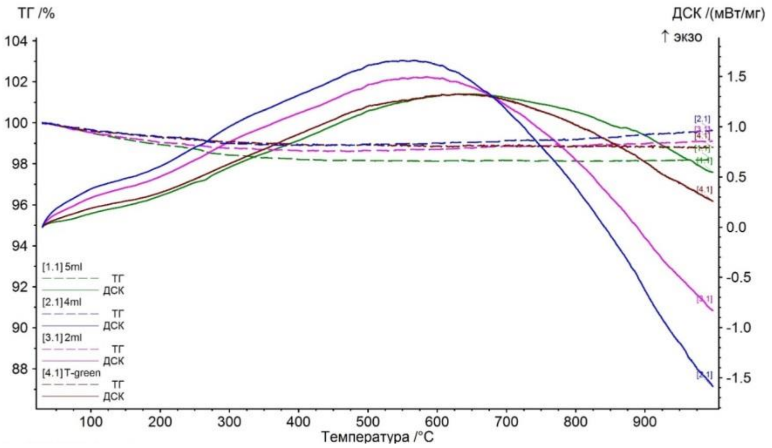


Figure 7: The results of thermal analysis of the mixtures of CW and zinc oxide. The curves of differential thermal analysis: 1.1 – 3%; 2.1 – 9%; 3,1 – 12% . 4.1 – source CW.

Exothermal effect with adding modifier acquires more pronounced character, that is indicative of proceeding the reaction of formation of zinc chromate. The temperature interval transfers to low temperature. X-ray structure analysis proves the formation of zinc chromate (figure 8).

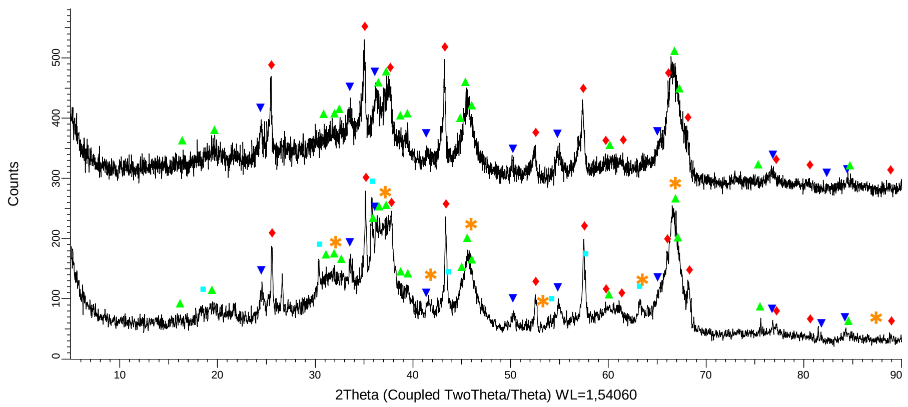


Figure 8: The results of X-ray structure analysis.

1 – CW 800°C 1 h, 2 – CW + zinc oxide

Table 3 illustrates the determination of physical and chemical characteristics of obtained products.

Table 3 Painting-technical parameters of products of thermal treatment with zinc oxide (3 hours of thermal treatment)

	Oil absorption, g/100g	Density, g/sm^3	Content of water-soluble substances, %	pH of water extract
ОП 800°C	28,8	3.23	1.99	6.35
ОП-Ц 3% 800°C	29.6	3.42	1.71	4.30
ОК-Цинк 3% 800°C	36.5	3.52	1.85	4.35
ОК 800°C	38.6	3.34	1.91	7.25

The increase of chromate content in the treated product (potassium chromate from potassium and zinc chromate compound containing in wastes on reaction with modifier – zinc oxide) lead to considerable improvement of inhibiting properties. The amount of current of corrosion in extracts EW-C – 5.7 mA/sm^2, CW-C – 6 mA/sm^2. (in the background electrolyte 20 mA/sm^2).

SUMMARY

The task of development of anticorroding pigments with low toxicity does not lose its urgency. The perspective direction is the use of different industrial wastes, specifically dead catalyst for obtaining inorganic pigments. The inorganic pigment for anticorroding compounds was obtained on the basis of chrome-containing catalyst on ceramic processing. It is shown that it leads to stabilization of the content of water-soluble substances and improvement of inhibiting properties by adding zinc oxide as modifier into charge makeup.

According to painting-technical figures the obtained products are up to quality that are demanded to the pigments in paint and varnish industry.

CONCLUSION

The industrial wastes contain valuable elements, in particular different metals, the reserves of which are exhaustible. The burial of such wastes is unreasonable from the point of view of stability of functioning of industrial complex on the whole. The industrial wastes are often multi-component mixtures of substances of heterogeneous chemical composition, having different physical and chemical properties. The processes of interaction between the components and the background objects and by-product assimilation bring a considerable uncertainty in chemical composition and material constitution of industrial wastes. The technologies of waste recycling to receive the products, specifically inorganic pigments, involve the complex of methods of processing with the use of different modifiers to obtain the needed complex of physical and chemical properties defining the functional characteristics of the target product.

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