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SOLVOTHERMAL SYNTHESIS OF BISMUTH ORTHOVANADATE AND ITS STUDY AS PIGMENT FOR PAINT -AND -VARNISH INDUSTRY

Bismuth orthovanadate was synthesized by solvothermal method. Physicochemical properties (oil-absorption power of I and II type, pH of the aqueous extract, the particle size and density) of the pigment obtained were determined. Corrosion stability of the synthesized pigment was studied by electrochemical method. It has been established that the chemical compound concerned is characterized by low solubility and can be used in the paint-and-varnish industry as a replacement for yellow lead-bearing and chromate pigments.

Introduction. Taking into account ecological requirements, the priority direction in the development of pigments for the paint-and-varnish industry is the production of nontoxic anti-corrosive substances that can replace lead-bearing and chromate pigments.

In our country pigments based on lead oxides, chromates, sulfates and molybdates are used as yellow ones. Bismuth orthovanadate can serve as an alternative to these substances. Despite the fact that the chemical compound involved is more expensive than lead compounds, bismuth orthovanadate has much higher coloring power and purer hue [1].

The key features of pigments are color, hiding power, coloring intensity, particle shape and size, wettability, oil absorption, weather resistance, as well as resistance to light and heat, chemical stability [1]. Pigment properties are generally determined by the conditions of synthesis. Anhydrous vanadates of many metals are typically produced by sintering their oxides, carbonates or nitrates with V_2O_5 or NH_4VO_3, which limits the availability of the synthesis process control, consumes much energy, and results in the formation of toxic gaseous by-products.

The application of solvothermal method using water solutions of electrolytes as precursors is potential for bismuth orthovanadate synthesis [2]. The method concerned makes it possible to control properties of the obtained disperse phase by varying synthesis conditions (nature and concentration of reacting substances and solvent, pH of the solution, temperature, processing stages etc.). It is simple and easy to implement, permitting to conduct the process under atmospheric pressure and at rather low (no more than 100°C) temperatures, no special equipment required.

The work performed was aimed at studying the possibility of applying solvothermal method for synthesizing bismuth orthovanadate to be used as an anti-corrosive pigment in the paint -and -varnish industry as well as at analyzing its physical and chemical properties.

Main part. Morphology and elemental composition of the synthesized products were studied via EDX method, using the JSM-5610 LV scanning electronic microscope provided with the EDX JED-2201 chemical electron microprobe analysis system within the accuracy of 0.5%.

The X-ray phase analysis (XPA) of the end-products was carried out on the D8 Advance Bruker AXS X-ray diffraction meter (Germany), using CuK_α – radiation. X-ray patterns obtained were processed by means of the EVA program included in the software package of the DiffractPlus diffractometer. The phase composition was determined using the International Radiographic Database, Powder Diffraction file.

Dispersion of pigments obtained was studied with the Analysette 22 laser microprobe analyzer of particle sizes, the instrument measurement range being 0.1–602.5 microns.

The true density was determined by bottle method according to GOST 21119.5. Oil absorption of pigments and pH of 10% water suspension were measured by standard techniques (GOST 21119.8 and GOST 21119.3, respectively).

Polarization measurements were carried out in the standard YaSE-2 three-electrode electrochemical cell with a platinum auxiliary electrode, using the IPC-ProM programmer device. Potentials were measured relative to the EVL-1M3 saturated silver chloride reference electrode and then recalculated in values for standard hydrogen electrode. 08kp steel (GOST 8832) was used for the working electrode. The visible surface of an electrode was 1.0 cm^2. Potentiodynamic anodic curves were taken off, with the potentials ranging from no-current to oxygen liberation ones.

Bismuth orthovanadate was synthesized by solvothermal method, water solutions of sodium vanadate (pH ≈ 13) and bismuth nitrate (pH ≈ 0) used as precursors

$$Bi(NO_3)_3 + Na_3VO_4 \rightarrow BiVO_4 + 3NaNO_3.$$

Various vanadate ions [3] are stable in water solutions, depending on pH value and vanadium compounds concentration. When mixing sodium vanadate and bismuth salt solutions, with Bi to V mole ratio being 1 : 1 and pH ≈ 0.6, bright yellow

colloidal solution is formed, and then friable amorphous mass is precipitated. It is established that when the product is formed in strong acidic media, the precipitated bismuth orthovanadate contains solid poly-vanadate impurities making the pigment brown-red.

To obtain single-phase product optimum conditions of bismuth orthovanadate formation were chosen, the process stages being the increase of pH colloidal solution value to 3.5 by adding 30% sodium hydroxide solution, 1hour mixing at room temperature, the incorporation of 1 N-solution of sodium hydroxide and setting pH value of the mixture to 6. It was determined that sharp rise of pH of the colloidal solution results in the formation of bismuth nitrate impurities and yellowish precipitate. To improve pigment quality and color, the pH adjustment was carried out gradually during 1h. The subsequent boiling of the obtained suspension for 3h produced fine powder of bismuth orthovanadate.

Using EDX method it has been established that the elemental composition of the obtained product may be presented in per cent by mass as: O – 20.54; V – 17.03; Bi – 62.44. The Bi to V mole ratio in the synthesized product is 0.9, which is probably the evidence of its having minor impurities of V_2O_5, bismuth meta- and poly-vanadates. According to the X-ray phase analysis (Fig. 1), within XPA error the obtained sample is single-phase one and has the structure of bismuth orthovanadate [4], which is indirect evidence that impurities in the synthesized product are X-ray amorphous. The $BiV0_4$ compound obtained is characterized by a tetragonal structure with the following parameters of the body-centered lattice: $a = (0.5138 \pm 0.0002)$ nm, $c = (1.1709 \pm \pm 0.0005)$ nm, tetragonality degree $c / a = 2.2788$, lattice cell volume (V) being $309.1 \cdot 10^{-3}$ nm^3.

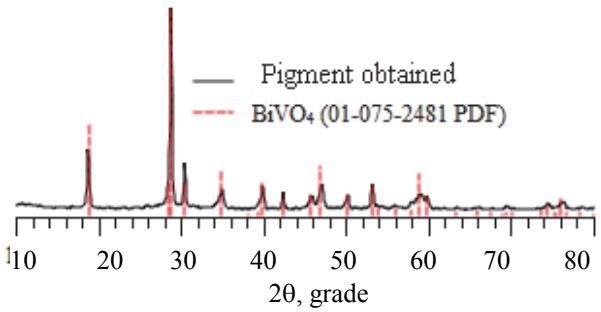

Fig. 1. X-ray pattern of the sample obtained

According to the data of scanning electron microscopy, the particles formed by the proposed solvothermal method are characterized by low degree of polydispersity and have the shape like the spherical one (Fig. 2).

Bismuth orthovanadate particle size distribution is presented in the form of integral and differential curves (Fig. 3). The data obtained show that particles of the synthesized product have sizes from 0.1 to 7.0 microns, and those of the main fraction (56.91%) – from 0.1 to 2.0 microns. As a rule, using pigments with such small particle sizes in the paint-and-varnish industry permits to significantly perfect the characteristics of finished goods (intensity, luster, hiding power) [1].

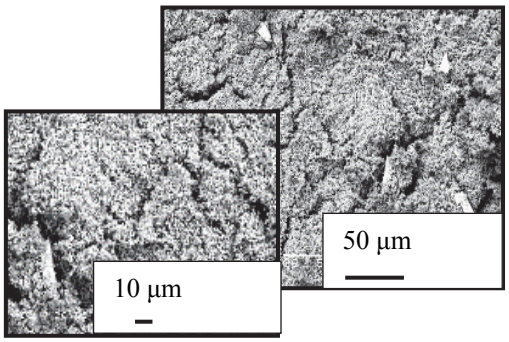

Fig. 2. Electron microscope image of the sample analyzed

Bismuth orthovanadate particle size distribution is presented in the form of integral and differential curves (Fig. 3). The data obtained show that particles of the synthesized product have sizes from 0.1 to 7.0 microns, and those of the main fraction (56.91%) – from 0.1 to 2.0 microns. As a rule, using pigments with such small particle sizes in the paint-and-varnish industry permits to significantly perfect the characteristics of finished goods (intensity, luster, hiding power) [1].

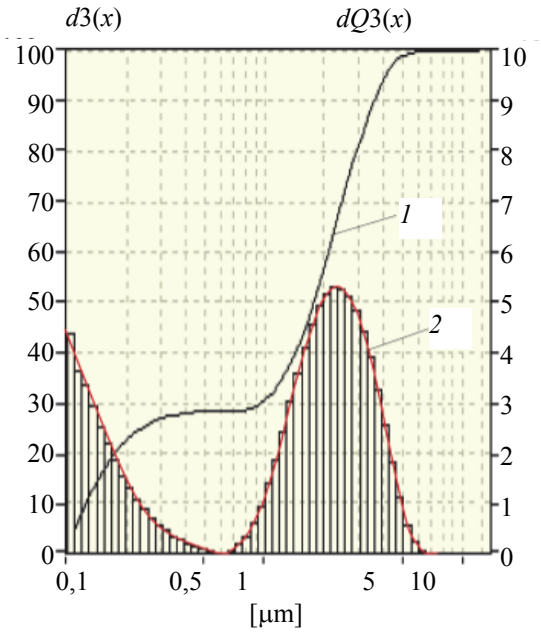

Fig. 3. Integral (*1*) and differential *(2)* dispersion curves for synthesized bismuth orthovanadate

Rapid analysis of inhibiting properties of the synthesized pigment was carried out by taking off anodic potentiodynamic curves on 08kp steel in 0.1 N-solution of Na_2SO_4 at the temperature of 20°C and at the potential scanning rate of 20 mV/s. The studies showed that by adding bismuth orthovanadate to an electrolyte, no-current potential shifts to an anodic potential region by 130 mV (Fig. 4).

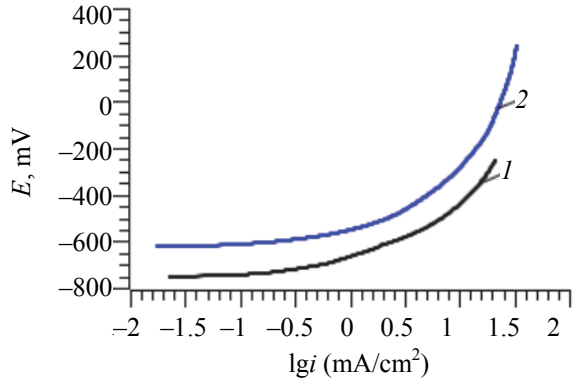

Fig.4. Anodic polarization curves in 0.1 N Na_2S0_4 without an inhibitor (*1*) and in pigment suspension (2)

Anodic polarization results in the electrode oxidation rate increase both in 0.1N-solution of Na_2SO_4, and in pigment suspension. However, at the same potentials the anodic steel oxidation rate in $BiVO_4$ suspension is 40–50% lower than in the absence of a pigment. Thus, the data obtained point to bismuth orthovanadate passivation effect on the steel substrate.

The study of physical and chemical properties of the pigment synthesized showed that the true powder density determined by bottle method is 6720 kg/m^3. pH value of $BiVO_4$ water suspension is equal to 6, which provides stability of the steel substrate being in contact with the pigment.The oil-absorption power of the bismuth orthovanadate sample obtained is like that of high-basic zinc chromates (30g/100g of a pigment) which in comparison with orthovanadate bismuth are light yellow and have low intensity and light-resistance [1]. The oil-absorption power of II kind that shows the amount of linseed oil necessary for obtaining ready to use paint (i.e. building paint) is 56g/100g of the pigment. Low values of I and II kind of the oil-absorption power of bismuth orthovanadate determine rather low cost of finish with it as a base.

The study of chemical properties of the bismuth orthovanadate obtained showed that it is almost insoluble in water and in organic solvents, but does dissolve in highly alkaline (pH > 13) and acidic (pH < 2) media. The data obtained point to good insulating properties of coatings based on the pigment synthesized.

Conclusion. The technique of bismuth orthovanadate solvothermal synthesis using sodium vanadate and bismuth nitrate water solutions as precursors has been proposed. Bright yellow powder with dimensional morphological characteristics, physical, chemical and inhibiting properties that meet the requirements for pigments used in the paint-and-varnish industry has been obtained. The investigations performed have permitted to come to the conclusion that it is possible to replace traditional chrome-containing anticorrosive pigments by less toxic bismuth orthovanadate in material formulations for paint-and-varnish industry.

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