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I. M. Zharskiy, I. I. Kurilo, Ye. V. Kryshilovich, D. S. Kharitonov
Belarusian State Technological University

SYNTHESIS OF PIGMENTS USING PRODUCTS OF VANADIUM CONTAINING INDUSTRIAL WASTE UTILIZATION

The results of studies of the elemental composition of vanadium-containing industrial waste have been presented. The expediency of its processing due to the profitability of production, the necessity of expanding the raw material base for short supply of vanadium and reducing of negative effects on the environment has been shown. Composition of products extracted from industrial vanadium-containing waste by hydrometallurgical method has been studied. The content of vanadium are based on V_2O_5 can reach more than 85 wt %, that meets specifications for this reagent. Solvothermal and sonochemical methods of bismuth vanadate synthesis from obtained vanadium (V) oxide have been developed. The phase and elemental composition of synthesized bismuth orthovanadate powders, their size, morphological and coloristic characteristics, physical and chemical properties: oil absorption, pH of the aqueous extract, particle size has been studied. It was shown that ultrasonic treatment of a suspension in the synthesis allows to intensify the process in 4–5 times, contributes to obtaining a smooth spherical particle shape, but also leads to an increase in particle size deteriorates powder and several coloristic properties of the pigment. The expediency of using products of vanadium-containing industrial waste treatment for the synthesis of paint pigments $BiVO_4$ has been shown.

Key words: vanadium-containing waste, recycling, solvothermal synthesis, pigments, composition, properties.

Introduction. Deficit of vanadium products in the Republic of Belarus as one of the main elements of steel alloying, raw material for production of catalysts, pigments, colored enamels, glazes and glasses has been estimated in dozens of tones. Spent vanadium catalysts of sulfuric acid production (SVC), hard combustion products of hydrocarbon at thermal power plants and products of deep oil processing: coke of thermoform-type cracking and tar are potential source of secondary vanadium-comprising raw material. Total volume of vanadium-comprising waste at the enterprises of the Republic of Belarus is currently about 11,000 tones. Concentration of vanadium in industrial waste is 10–100 times higher than its content in traditional crude ore (Table 1).

Apart from high content of vanadium compounds in vanadium-comprising industrial waste, their importance as a source of secondary raw material lies in the fact that it is not required to use any other additional stages for their production, enrichment, agglomeration, domain melting and vanadium removal from cast iron in converters.

Importance of processing of vanadium-comprising industrial waste is provided not only by production profitability but also by deteriorating ecological situation in the Republic of Belarus. If earlier enterprises were able to remove vanadium-comprising waste into the Russian Federation for processing but after Basel Convention coming into force on the control of transboundary transportation of hazwaste and its disposal, domestic enterprises have to organize a long-term storage of this type of waste referring to the second class of danger on its own territory. Storage of vanadium-comprising waste is interconnected with expropriation of lands under sliming and tailing storage facility, pollution of surface-water flow and underground waters, surface atmosphere and soils with toxic components spreading onto the considerable distance.

Thus, development of effective ways of processing of vanadium-comprising industrial waste and efficient use of extracted materials provide solving of two main tasks: expansion of raw material base for metal in very short supply and decrease of ecological loading on environment.

Main part. Belarusian state technological university has developed hydrometallurgical methods of isolation of vanadium-comprising components out of industrial waste that are formed at enterprises of the Republic of Belarus: SVC such as sulfovanadate on silicagel [1, 2] and ash residue of vanadium-comprising slimes of TPP [3, 4]. Proposed methods permit to isolate 95–98% of vanadium, containing in industrial waste. Vanadium content in the product isolated from leaching solutions in the course of thermohydrolysis depends on the content of the initial waste and method of processing (Table 2) [1–4].

According to the provided data, the content of vanadium in isolated product expressed in terms of V_2O_5 can reach more than 85 mas. %, that meets the demands of TS for technical vanadium oxide (V). Thus, it was important to study possible methods of usage of obtained secondary vanadium-comprising compounds.

Table 1

Averaged compositions of industrial vanadium-comprising waste

Type of waste	Content of elements, wt %														
	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	V	Fe	Cu	Zn	Ni
Spent vanadium catalysts of OJSC "Grodno "Azot" (Grodno)	10.30	43.39	2.01	–	<1	18.9	10.2	–	9.09	<1	4.20	<1	<1	<1	–
Vanadium-comprising slimes of CHPP-3 (Minsk)	19.83	23.68	–	1.03	0.54	1.46	–	–	–	48.6	0.17	4.60	–	–	–
Vanadium-comprising slimes of RUE "BrestEnergo" branch "Berezovskaya SDPP" (Beloozersk)	10.08	37.74	–	4.11	0.49	9.69	0.40	–	–	14.1	1.21	22.1	–	–	–
Oil-burning ash of RUE "BrestEnergo" branch "Berezovskaya SDPP" (Beloozersk)	20.92	34.05	–	0.57	0.99	1.97	12.9	19.0	–	19.0	1.77	7.79	–	–	–
Oil-burning ash of PMC "Vitebsk confectionary works "Vitba" (Polotsk)	6.46	33.84	0.17	0.54	0.9	2.25	17.2	–	0.63	24.7	2.94	6.96	0.52	1.74	1.08

One of the upcoming trend of application of vanadium-comprising derived products of industrial waste is synthesis on their base of compounds suitable for usage as pigments for paints and varnishes industry. In a number of countries due to reinforcement of environmental requirements usage of yellow pigments comprising lead and chrome compounds is limited and there is an active search for alternative less toxic compounds such as bismuth orthovanadate that has higher dyeing ability and more perfect yellow colour [5, 2].

Currently for synthesis of vanadates hyperthermal and hydrochemical methods are used [6, 7]. As a rule, baking of oxides, carbonates or nitrates of metals with V_2O_5 or NH_4VO_3 requires high power consumption, results to formation of vanadium compounds admixtures in lower oxidation degree and toxic gaseous by-products. Application of solvothermal method used as precursors of aquosystem is more promising for synthesis of orthovanadates [6].

Vanadium oxide (V) isolated from SVC by hydrometallurgical method and containing 48.0 wt % of vanadium, expressed as V_2O_5 and equals to 85.7 wt % and also $Bi(NO_3)_3 \cdot 5H_2O$ of "c. p." brand was used for synthesis.

Morphology and elemental composition of synthesized products have been studied by scanning electron microscopy (SEM) and energy-dispersive x-ray microanalysis (EDX) on scanning electron microscope JSM-5610 LV with EDX JED-2201 system within the accuracy of up to 0.5 wt %.

X-ray phase analysis (XPA) of end-product has been carried out by diffractometer D8 Advance Bruker AXS (Germany) with CuK_α-rays. Decoding of obtained diffractograms has been carried out by specially conFigured software Crystal Impact Match 2 suitable for qualitative and quantitative measurement of phase compositeon and crystal lattice parameters and in accordance with reference of Crystallography Open Database (COD).

Pigments oil-adsorption and pH of 10% water suspension of bismuth orthovanadate samples have been determined by standard methods (NSS 21119.8 and NSS 21119.3).

Studies of dispersiveness of the obtained pigments have been carried out by laser microanalyzer of particle size, Analysette 22. Meter range of the device is 0.1–602.5 μm.

Coloristic properties of the obtained pigments have been measured by spectrophotometer ColorDialog II by reflected light. Measurements included determination of color density and tristimulus values in the system of Lab (CIELAB). Measure methods include:

1) stirring of pigment in agate mortar till homogeneous mixture with minimal possible grain-size of testing powder;

2) coating of supported-surface with pigment powder and layer solidification till obtaining even smooth surface as thick as not less than 5 mm;

3) color specification of pigment in three points.

Table 2

Compositions of vanadium-comprising products isolated by processing of industrial waste

Type of vanadium-comprising waste	Method of recessing	Method of isolation of vanadium compounds out of solutions	Content of elements, wt %													
			O	Na	Mg	Al	Si	S	Cl	K	Ca	V	Fe	Cu	P	Zn
Ash residue of vanadium-comprising slimes of TPP	HCl leaching with oxidant	Thermohydrolysis	24.8	0.8	0.4	0.5	0.2	0.6	0.3	0.1	4.2	26.2	36.3	–	5.6	–
	HCl two-stage leaching with oxidant	Thermohydrolysis	42.6	–	–	–	2.0	0.8	–	4.9	–	48.0	1.7	–	–	–
	Oxidizing burning and H_2SO_4 leaching	NH_3 water solution deposition	38.5	17.7	1.5	2.3	5.3	0.8	–	–	15.4	14.5	1.6	0.6	–	1.8
	Oxidizing burning and H_2SO_4 two-stage leaching	NH_3 water solution deposition	40.4	4.8	10.1	–	2.6	1.0	–	2.8	6.0	32.2	–	–	–	–
Spent catalysts of sulfuric manufacturing such as sulfovanadate on silicagel	Hydrometallurgical method of processing [1, 2]	H_2O_2 oxidation, thermohydrolysis	42.6	–	–	–	2.0	0.8	–	4.9	–	48.0	1.7	–	–	–
		$(NH_4)_2S_2O_8$ oxidation, thermohydrolysis	42.1	–	–	–	1.0	0.6	–	5.2	–	48.5	2.6	–	–	–
	Electrochemical method of processing [1]	Anodic oxidation	40.5	–	–	–	–	–	–	3.0	–	47.7	9.1	–	–	–
		Cathode reduction	43.1	1.0	–	4.7	–	4.2	–	7.0	–	39.0	1.0	0.1	–	–

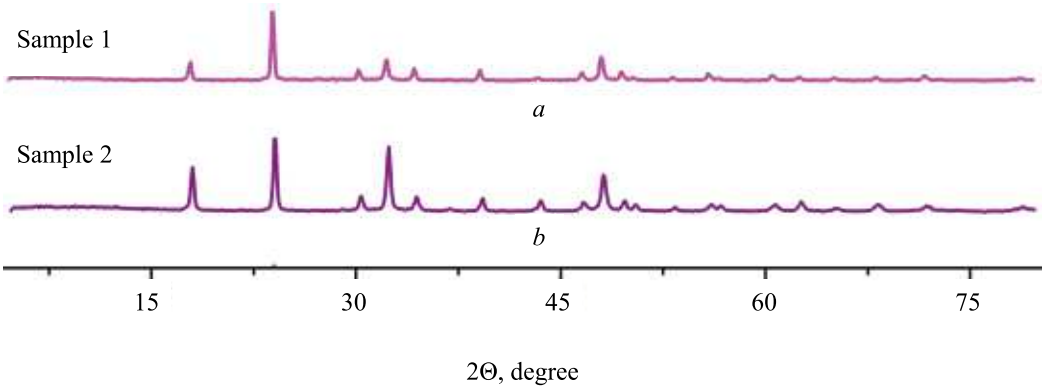


Fig. 1. X-ray diffractograms of bismuth orthovanadate samples:
a – obtained without US;
b – obtained with US processing of suspensions

Synthesis of bismuth orthovanadate included the following stages:

1) dissolution of vanadium-comprising product in sodium hydroxide solution (pH ≈ 13) and filtrate separation containing sodium orthovanadate [8], out of impurities of alkali-insoluble admixture;

2) intermixture of alkaline solution of sodium vanadate with acidic solution of bismuth salt in mole ratio of n(Bi):n(V) = 1:1 with forming of bismuth orthovanadate:

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

3) correcting of pH factor of the obtained mixture till 3.5 by 30% sodium hydroxide solution;

4) stirring within an hour at room temperature;

5) step-by-step administration of 1 n. sodium hydroxide solution and obtaining of pH level of the mixture equals to 6 within an hour;

6) heating of the mixture and keeping it at boiling temperature within three hours;

7) cooling of the mixture till room-temperature, filtration, elutriation by distil water and its drying at the temperature of 90°C.

Total duration of synthesis without time for drying was about 9 hours. As a result, reed yellow bismuth orthovanadate powder has been obtained (Fig. 1, *a*).

With the purpose of synthesis intensification after draining of water solutions of precursors (stage 2) correcting of pH factor of the mixture to 6 has been carried out. Then, within 7 minutes, sonochemical processing by ultrasonic (US) device with piezoelectric transmitter at ultrasonic field capacity of 630 W, operating rate of – 22 ± 10% kHz, amplitude of vibration – not less than 40 μm has been implemented. Obtained bismuth orthovanadate (Fig. 1, *b*) has been isolated in accordance with the stages of synthesis of 6 and 7. Duration of sonochemical synthesis without time for drying was about 2 hours.

According to the data of scanning electron microscopy (Fig. 2), particles formed under the influence of US have more perfect spherical shape in contrast to the particles obtained without sonochemical processing.

According to x-ray phase analysis (Fig. 1) obtained samples are single-phased ones and have a structure of bismuth orthovanadate with tetragonal system. Calculated parameters of bulk-centered lattice represented in Table 3 coincide with literature data [6]. According to submitted data, US processing almost have no influence on parameter value from crystal lattice but provides some decrease of parameter *a* and volume *V* of elementary cell.

According to elementary analysis of obtained compounds, mole ratio n(V):n(Bi) is 1.06:1.00 and 1.02:1.00 for samples 1 and 2 correspondently, it can prove the presence of some admixture of polyvanadates in their composition [8].

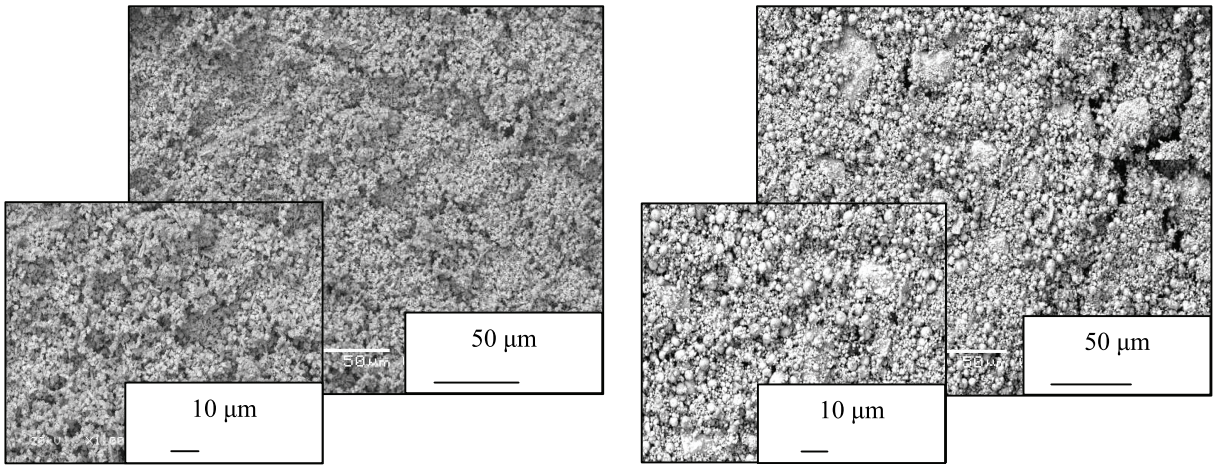
To find the possibility of the usage of synthesized samples $BiVO_4$ as pigments for pains and varnished industry their physicochemical properties have been studied (Table 4).

Table 3

Parameter value (*a*, *c*), of center-to-center spacing (*c* / *a*) and volume (*V*) of elementary cell of synthesized compounds of bismuth orthovanadate

Sample	*a*, Å	*c*, Å	*c* / *a*	*V*, Å^3
1	7.306(2)	6.458(7)	8.839	344.7
2	7.296(1)	6.454(1)	0.8846	343.5

According to the obtained data (Table 4), particles of bismuth orthovanadate synthesized without US processing have uniform grading: power fraction (57%) is from 0.1 to 2.0 μm. Application of sonochemical processing results to the increase of particles size of the power fraction (51%) to 20–50 μm.



a *b*

Fig. 2. Electron microscope image of bismuth orthovanadate samples:
a – obtained without US; *b* – obtained with US processing of suspensions

Table 4

Physical properties of synthesized pigments

Index	Number of sample	
	1	2
Dominating size of particles, μm	0.1–2.0 (57%)	20–50 (51%)
water suspension pH	6	6
Oil-adsorption of the I type, g/100 g	31	20
Oil-adsorption of the II type, g/100 g	57	36

Oil-adsorption of the I and II type for the pigment obtained without US is correspondently 31 and 57 g per 100 g of flax oil that is equal to oil-adsorption of chrome-bearing pigments [9].

Sonochemical processing in the course of synthesis of bismuth orthovanadate results to the decrease of its oil-adsorption by 63–65%. Decrease of oil-adsorption can be explained by the increase of particles size and degree of heterodispersion powders $BiVO_4$ synthesized with the help of US. In the course of wetting of the obtained pigment by oil smaller particles can be placed between bigger ones that results to the decrease of voids volume between particles and therefore to the decrease of oil-adsorption.

It is established that pH of suspension water extract of synthesized samples is 6. This provides one of the conditions of corrosion resistance of steel articles that are in contact with paint material produced on the basis of obtained vanadium-comprising pigments.

Without sonochemical processing the reed yellow samples have been obtained, with US processing – light brown. In the course of studying of coloristic properties of the obtained pigments comparison and choice of the most suitable color have been carried out by comparison of color coordinates obtained during the tests with coordinates from the catalogues (Table 5).

According to the provided data color coordinates of the obtained pigments corresponds to the colors from graphic printing catalogue Pantone and technical catalogue RAL. According to the color $BiVO_4$ powders obtained by solvo-thermal method are close to the samples of comparison. Using US processing the color of the pigment became brown and also derating of *L*-coordinate determing color intensity has been observed.

Conclusion. According to the completed tests vanadium content in spent vanadium catalysts such as sulfovanadate on silicagel and ash residue of vanadium-comprising slimes of TPP forming at enterprises of the Republic of Belarus is 0.17–4.20 wt %. It is 10–100 times higher than its content in crude ore and therefore provides reasonability of processing of this type of waste.

Application of hydrometallurgical methods for processing of vanadium-comprising industrial waste allows receiving final product in which vanadium content expressed as V_2O_5 may be more than 85 wt %.

Synthesized by solvo-thermal and sonochemical methods using vanadium-comprising derived products of SVC samples of bismuth orthovanadate are single-phased with tetragonal system. Calculated parameters of bulk-centered lattice coincides with literature data. US processing almost has no influence on parameter value from crystal lattice but provides some decrease of parameter *a* and volume (*V*) of elementary cell.

Table 5

Coloristic properties of the obtained pigments

Pigment	Number of test	Color coordinates						Catalogue color number	
		L	a	b	$\overline{L}$	$\overline{a}$	$\overline{b}$	RAL	Pantone
$BiVO_4$ (c. p., comparison sample)	1	62.23	25.12	72.48	62.87	23.79	71.20	1028	137C
	2	63.23	23.12	70.58					
	3	63.15	23.14	70.54					
1	1	73.25	21.21	75.36	73.58	20.86	77.39	1003	130C
	2	74.25	20.12	77.58					
	3	73.25	21.25	79.24					
2	1	36.69	18.56	31.63	36.24	18.05	31.59	8003	463C
	2	36.78	17.58	31.56					
	3	37.69	21.08	17.56					

Particles of bismuth orthovanadate synthesized by solvo-thermal method have uniform grading in which dominating size of power fraction (57%) is from 0.1 to 2.0 μm. Usage of sonochemical processing allows intensifying synthesis by 4–5 times and results to the formation of particles of more perfect spherical shape, increase of their size to 20–50 μm (51%), and also to polydispersity degree. This, in its turn, provides the decrease of oil-adsorption of $BiVO_4$ powders obtained with US by 63–65%; pH of water extract of synthesized samples is 6.

Powders of bismuth orthovanadate obtained without US processing are reed yellow, by sonochemical method – light brown. According to the results of studies of coloristic properties of synthesized samples it has been found out that their color coordinates correspond to the colors currently used in paint (catalogue RAL) and printing (catalogue Pantone) industry.

Thus, synthesized on the basis of the derived products of vanadium-comprising industrial waste bismuth orthovanadate powders according to their dimensional and morphological and coloristic properties and also physical and chemical properties are as good as samples obtained from the reagents of the brand “c. p.” and can be recommended for usage as yellow pigments in formula of paint-and-lacquer materials.

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Information about the authors

Zharskiy Ivan Mikhailovich – Ph. D. Chemistry, professor, Rector of Belarusian State Technological University. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: root@belstu.by

Kurilo Irina Iosifovna – Ph. D. Chemistry, associate professor, Head of the Department of General and Inorganic Chemistry. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: kurilo@belstu.by

Kryshilovich Yelena Vladimirovna – associate, Department of General and Inorganic Chemistry. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: kryshilovich@belstu.by

Kharitonov Dmitriy Sergeevich – undergraduate student, Department of Chemistry, Electrochemical Production Technology and Materials for Electronic Equipment. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: kharitonov@belstu.by

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