

Colour modifiers of zirconium-vanadium pigments on a ZrO_2 basis

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The synthesis of yellow baddeleyite pigments involves a phase transition of ZrO_2 , which facilitates the process of incorporating vanadium chromophore into its lattice, and occasionally also modifiers, such as oxides of trivalent elements, either chromophoric or non-chromophoric. Depending on the type of the modifier used – an oxide of indium, yttrium, gallium or thallium – the yellow-green colour of the two-component ZrO_2 -V pigment may be changed smoothly into yellow or yellow-orange. The temperature of the synthesis of ZrO_2 -based pigments ranges from 1050 °C to 1325 °C, depending on the properties of the substrates, such as a non-oxide form of the materials – ZrOCl_2 , $\text{Zr}(\text{SO}_4)_2$, certain additives (*e.g.* Bi_2O_3). Raising the synthesis temperature over 1400 °C has no visible effect on the colour quality of the pigment, as it depends on the concentration of the vanadium chromophore in the ZrO_2 structure. The article describes the effect of the synthesis temperature and modifying additives on the effectiveness of incorporating vanadium into the ZrO_2 lattice and, consequently, on the colour properties of the pigment.

Keywords: *baddeleyite pigment; vanadium chromophore; modifiers; colour parameters*

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1. Introduction

High-temperature pigments called zirconium-vanadium yellows, first produced from baddeleyite in the 1940s, were an alternative for low-temperature and toxic antimony-lead and tin-vanadium yellows [1, 2]. Similarly to the tin-vanadium yellow, the yellow colour of the pigment comes from vanadium in an oxidation state of +5 [3, 4].

It was believed that the colour of the pigment was associated with a surface layer of vanadium pentoxide deposited on the grains of zirconium dioxide since a yellow precipitate of the compound was isolated in the course of pickling with hydrochloric acid [5]. At the same time, despite pickling, the rest of the pigment retained the yellow colour whose intensity grew with an increase of the crystallite size. The fact was interpreted in favour of the so-called solution theory, assuming that the pigment was a solid solution of vanadium pentoxide in a matrix of zirconium dioxide. The hypothesis was confirmed by an X-ray identification of monoclinic zirconium

dioxide both before and after a thermal synthesis of the pigment [5, 7].

An important stage in the pigment synthesis is a formation of an unstable phase of zirconium pyrovanadate (ZrV_2O_7) [6, 7] at the temperature of approximately 800 °C, that undergoes decomposition at over 1000 °C accompanied by evolution of fine-grained highly reactive ZrO_2 crystallites subject to phase transition. A defect structure and increased reactivity of zirconium dioxide due to the polymorphic transition of a monoclinic ZrO_2 phase into a tetragonal phase and the volume change associated with the transition is conducive to incorporation of chromophoric vanadium ions $\text{V}(+5)$. The remaining, not built-in vanadium pentoxide is occluded by ZrO_2 crystals in the course of formation their aggregates of 7–10 μm in size [8]. The sheath of ZrO_2 crystals protects the chromophore from an aggressive chemical action of glaze components and thus the pigment colour is intense and stable. This is confirmed by the fact that colour intensity is reduced in the case of particularly fine-grained pigments.

An evidence of the crucial importance of the phase transition of ZrO_2 for the mechanism of pigment production is the fact that no success has been

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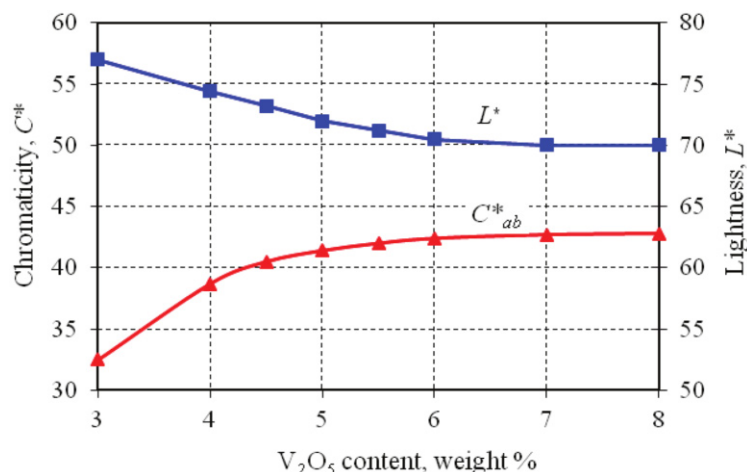


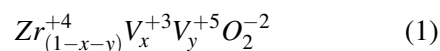
Fig. 1. The relationship between chromaticity C^*_{ab} and lightness L^* of a yellow zirconium-vanadium pigment and the V_2O_5 concentration in the raw material batch [9].

achieved in producing a yellow pigment either from stabilized or from unstabilized zirconium dioxide at lower temperatures than the temperature of the transition [5].

A raw material batch for pigment synthesis usually consists of ZrO_2 and vanadium based material NH_4VO_3 or V_2O_5 in the amount of 5–10 wt.%. Studies [9] have demonstrated that a good pigment colour requires a significant excess of vanadium chromophore in the raw material batch in relation to its quantity incorporated in the ZrO_2 structure. Chromaticity C^*_{ab} of the pigment colour rises with increasing the quantity of the chromophoric material in the raw material batch up to 6 wt.%. Also, lightness L^* decreases within that range, which is an evidence of an improvement of functional parameters of the pigment. Chromophore quantities larger than 6 wt.% in the raw material batch do not have any visible effect on pigment parameters: the correlation curves of chromaticity C^*_{ab} and lightness L^* are almost parallel (Fig. 1).

At the concentration of 5–8 wt.% of the chromophoric material in the batch, only up to 0.5 wt.% is used for building the pigment (as calculated for V), depending on firing conditions [10]. The pigment colour has a characteristic greenish-khaki hue of various intensity [5, 11, 12] caused by incorporating into the baddeleyite lattice, besides “yellow ions” of vanadium in an oxidation state of +5, also

vanadium ions in an oxidation state of +3 in order to compensate the charges of two zirconium ions in an oxidation state of +4. The pigment may be then described, for example, with the following generalized formula [13]:



Due to the fact that vanadium may occur in various oxidation states depending on the synthesis conditions, the ZrO_2 lattice may incorporate vanadium ions in oxidation states +4, +5 and +3, producing blue, yellow and green colours, respectively [14]. Vanadium ions in an oxidation state of +3, responsible for the green colour, may be prevented from being incorporated into the ZrO_2 lattice by means of introducing other modifier ions with a similar electron configuration, such as In^{3+} , Ga^{3+} [11, 15], Y^{3+} [5]. Embedding such an ion into the pigment lattice may result in changing its colour from yellow-green into yellow or yellow-orange [9, 14, 16].

The most frequently used form of the modifier is an oxide. Indium oxide is particularly effective as a colour modifier at a concentration of 0.1–1.0 wt.% in the raw material batch. Increasing the share of In_2O_3 over 1 wt.% does not improve chromaticity nor intensity of the pigment, and its addition of over 1.6 wt.% has a negative effect on the parameters [11]. A good colour modifier is gallium oxide, Ga_2O_3 [11]. In the case of bismuth oxide, a clear

bright yellow pigment colour depends on the relationship between the compound and vanadium oxide in the material batch. Particularly interesting colour properties occur when the molar proportion of $V_2O_5:Bi_2O_3$ equals (1.1:1.0)–(1.0:1.1) [11, 12, 17]. It is also possible to modify a pigment colour through an isomorphous substitution of a portion of zirconium dioxide with tin dioxide [5]. Solutions of that type display high colour stability within a wide temperature range. Raw material batches may be prepared in a traditional way, by means of co-precipitation or by the sol-gel method. No case has been recorded, however, of that type of pigment having been obtained beyond laboratory conditions.

Information has been published [18] on pigment synthesis on a ZrO_2 basis with the participation of lanthanides: Ce, Pr, Nd, Y, Er, Tb, Dy. Two of the obtained pigments displayed the best colour quality: a yellow pigment with a share of 15 molar % of praseodymium chromophore Pr_6O_{11} , and a pink pigment with a formula: $Zr_{0.9}Er_{0.1}O_2$. The colour effects of the pigments, described for an organic matrix and for a glaze, occur only at concentrations of over 15 wt.%, which determines their low intensity and, therefore, low usefulness for practical purposes.

The aim of the present study was to increase chromaticity and intensity of a yellow pigment with a ZrO_2 lattice by means of modifying the raw material batch with yttrium and indium oxides, with a simultaneous reduction of the concentration of vanadium compounds in the technological liquid waste.

2. Experimental part

Raw material batches of fixed composition formulas were blended and then fired, under lids, in ceramic refractory covers at the temperature of 1200–1400 °C, during a retention period of 1 hour. The sintered product was dry- or wet-ground in an agate mill until an identical grain size was obtained in each case: $d_{50} = 7 \pm 0.5 \mu m$. Due to a short (10 minutes) grinding time of the sinter, the amount of the additionally ground up SiO_2 was small and it did not have any substantial effect on the pigments colour, which was evaluated in the glaze. The average grain

size d_{50} was determined using the laser method on a Mastersizer Microplus apparatus manufactured by Malvern. Three types of pigment samples were prepared for tests:

- products after calcination, dry-ground (marked “S”),
- ground sintered products washed with cold water (marked “W”),
- ground pigments, hot-pickled with 30 wt.% nitric acid (marked “K”), containing vanadium chromophore only in the form that was built into the structure and occluded between ZrO_2 crystallites.

Determination of vanadium concentration in the samples prepared in the form of “a melted down pearl” was performed by XRF with dispersion of wave length WD-XRF (PANalytical MagiX PW2424). The measurement conditions were as follows: $K\alpha$ line, voltage – 50 kV, current intensity – 48 mA, the lamp with a rhodium anode. “The pearl” was prepared for the analysis by melting a mixture of 1 g of the tested pigment and 10 g of lithium metaborate and lithium tetraborate fluxes in the proportion of 1.7:3.3.

A quantitative and qualitative analysis of the phase composition was performed by the method of X-ray diffraction, with a D8 Discover X-ray diffractometer manufactured by Bruker AXS. The data were recorded within 2θ range of 4–100° using $CuK\alpha$ radiation, with steps of 0.02° and counting time 1.25 s/step. The recorded diffractograms were analysed on the basis of standards supplied by the International Centre for Diffraction Data (ICDD). The quantitative analysis of individual phases and their lattice parameters was performed with the use of Rietveld method in TOPAS software.

For an evaluation of pigment colours, colour glazes were prepared by grinding sodium-boron transparent frit used for tile glazing, with 5 wt.% of the pigment (of the grain size $d_{50} = 7 \pm 0.5 \mu m$), spreading the suspension on a flat bisque surface with a special template and firing it in a laboratory furnace at the temperature of 1100 °C in a cycle of 40 minutes.

Measurements of glaze colours were performed with a MINISCAN spectrophotometer manufac-

Table 1. Properties of the zirconium material ZrO₂ used in the study.

Properties	Trade symbol of the raw materials
	ZrO ₂ -S
Chemical composition, wt. %	
– ZrO ₂ + HfO ₂	99.65
– SiO ₂	0.09
– Na ₂ O	0.09
– SO ₂	0.17
Specific surface, S, m ² /g	5.40
Parameters of an elementary cell	
– <i>a</i> ₀ , Å	5.1508±0.0002
– <i>b</i> ₀ , Å	5.2022±0.0002
– <i>c</i> ₀ , Å	5.3175±0.0002
– <i>V</i> ₀ , 10 ⁶ pm ³	140.68
– β, deg	99.15

tured by HunterLab and the results were expressed with parameters L^* , a^* , b^* , signifying, in the CIELab system, as follows: L^* – lightness, brightness, a^* – positive – red, negative – green, b^* – positive – yellow, negative – blue. C_{ab}^* stands for chromaticity, which is calculated according to the formula:

$$C_{ab}^* = \sqrt{(a^*)^2 + (b^*)^2} \quad (2)$$

The formula

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3)$$

determines the difference of colour between two test samples or between a test sample and a standard.

A glaze colour was interpreted in terms of quantitative and qualitative fractions of particular raw materials as well as of the chemical composition and crystal structure of the pigment.

The zirconium material used in the study was a fine-grained variety of commercial zirconium dioxide manufactured by SEPR (France) (Table 1).

3. Results and discussion

A small portion of vanadium chromophore introduced into the raw material batch was incorporated into the pigment's structure. The remaining, prevalent amount of the chromophore, separated from the

pigment in the course of its wet grinding, was transferred to the technological sewage and constituted a troublesome waste due to the toxicity of soluble vanadates.

The effectiveness of incorporating vanadium chromophore into the ZrO₂ lattice was studied in dependence on the synthesis temperature and on the type of modifiers added to the raw material batch (P-0) with a composition of 94 weight parts of ZrO₂ and 7.71 weight parts of NH₄VO₃, which corresponded to 6 weight parts of V₂O₅ (or 3.36 weight parts of V). A measure of effectiveness was vanadium concentration in the pigment's structure and its colour parameters (Table 2).

The highest chromophore concentration in the structure – 0.495 wt.% was discovered in the pigment fired at the temperature of 1300 °C. The pigment displayed, consequently, the highest chromaticity: $C_{ab}^* = 45.81$, which indicated its best functional parameters. In addition, the lowest concentration of vanadium compounds in the technological waste was observed. Pigments fired at lower (1250 °C) and higher (1400 °C) temperatures were of inferior quality. There was a substantial difference in colour (in glazes), reaching, respectively: $\Delta E^* = 5.59$ and 2.81. The effectiveness of incorporating chromophore into the structure and reducing the concentration of vanadium compounds in the waste was dependent on the temperature of raw material firing.

In the process of pigment production on ZrO₂ basis, the modifiers were introduced into the raw material batch in the form of oxides: In₂O₃ and Y₂O₃, capable of altering the colour properties of the pigment. Zirconium dioxide impurities *e.g.* silica, titanium dioxide, in extreme case, may result in modifications to the color of the product.

Tests of a raw material batch: ZrO₂-V₂O₅ (P-0) with an addition of In₂O₃ within the range of 0.58–6.45 wt.% revealed that only small quantities (1.0–2.0 wt.%) of In₂O₃ had an advantageous effect on the pigment's colour with the fraction of vanadium chromophore remaining unchanged [19]. The pigments obtained in this way displayed higher chromaticity and intensity than the unmodified two-component pigments ZrO₂-V₂O₅. The tendencies of parameter change with different shares (3–7 wt.%)

Table 2. A relationship between the properties of the pigment P-0 ($\text{ZrO}_2\text{-V}$) and the temperature of firing a raw material batch with chromophore content of 6 wt.% of V_2O_5 (3.36 wt.% of V).

No	Determinations	Firing temperature [$^{\circ}\text{C/h}$]			
		1250/1	1300/1	1350/1	1400/1
1	Parameters of glaze colours:				
	– L^*	69.04	70.11	70.01	71.59
	– a^*	5.32	6.48	6.31	4.09
	– b^*	40.08	45.45	44.01	41.39
	– C_{ab}^*	40.43	45.81	44.46	41.89
	– ΔE^*	5.59	–	1.45	2.81
2	Fraction of vanadium compounds in liquid waste [V, g/100 g of pigment]:				
	– after washing the pigment with distilled water,	0.041	0.130	0.126	0.458
	– after pickling with nitric acid	2.981	2.730	2.759	2.504
3	Vanadium concentration in the pigment's structure, [V, wt.%]	0.332	0.495	0.471	0.391
4	Vanadium balance (item 2+3), [V, wt.%]	3.354	3.355	3.356	3.353

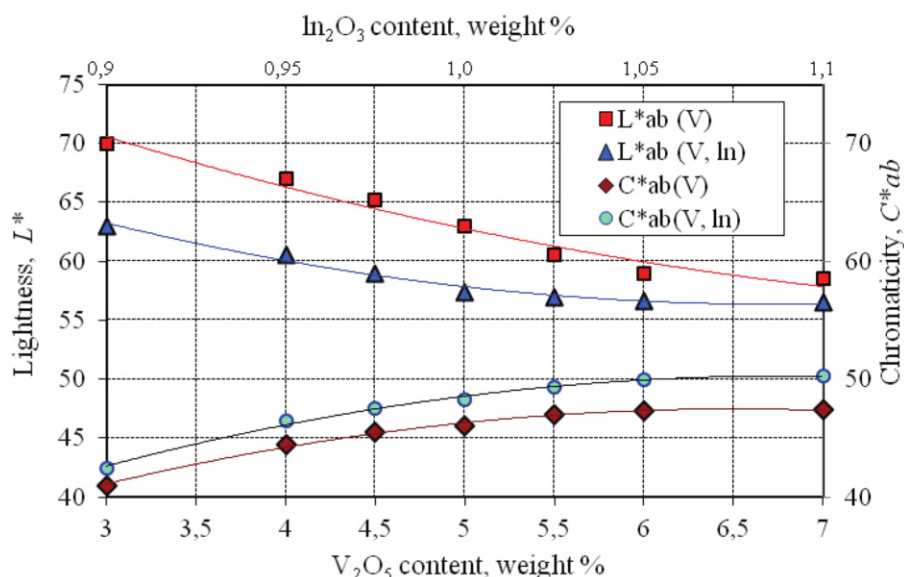


Fig. 2. A diagram of changes of chromaticity C_{ab}^* and lightness L^* in pigments modified with indium oxide and in unmodified pigments.

of vanadium chromophore V_2O_5 in the raw material batch have been presented in Fig. 2.

Analyses of the crystallographic structure of the pigments modified with In_2O_3 revealed that the content of ZrO_2 was higher than in an unmodified pigment (P-0) (Table 3). V_2O_5 did not occur, and the content of ZrV_2O_7 was reduced in favour of the phase of InVO_4 , whose quantity increased from

0.9 wt.% to 1.3 wt.% with an increasing content of indium oxide in the raw material batch. Respectively, an increase in chromaticity and colour intensity was observed while the concentration of vanadium chromophore had similar values (0.32–0.35 wt.% of vanadium ions).

An increase of the pigment colour chromaticity with the level of vanadium chromophore built into

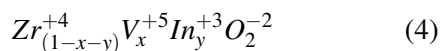
Table 3. Properties of pigments fired at 1300 °C/1 h on the basis of the raw material batch P-0 modified with indium oxide.

No	Properties	Pigment symbol					
		P-0	P-2	P-3	P-4		
1	In ₂ O ₃ content in the raw material batch, wt. %	–	1.0	1.5	2.0		
2	Quantitative phase composition of the pigment washed with water, wt. %						
	– ZrO ₂ monoclinic	91.8±0.3	96.1±0.7	94.9±0.7	94.1±0.7		
	– ZrV ₂ O ₇	4.5±0.4	2.2±0.3	1.9±0.3	2.2±0.4		
	– V ₂ O ₅	1.5±0.1	–	–	–		
	– NaV ₆ O ₁₅	1.6±0.6	1.3±0.5	2.1±0.6	3.1±0.9		
	– InVO ₄	–	0.9±0.3	1.1±0.3	1.3±0.3		
3	Vanadium content, V, wt. %:						
	– in a sintered product,	2.71	2.73	2.82	2.88		
	– in a pigment washed with water	2.30	2.48	2.52	2.55		
	– built into the structure	0.34	0.33	0.32	0.34		
4	Colour parameters of glazes:		<i>a</i>	<i>a</i>			
	– <i>L</i> [*]	80.67	74.79	77.01	73.84	75.06	77.95
	– <i>a</i> [*]	1.03	11.10	8.50	11.60	9.32	7.62
	– <i>b</i> [*]	44.39	48.19	49.25	46.92	48.17	46.42
	– <i>C</i> _{ab} [*]	44.40	49.45	49.98	48.33	49.06	47.04

^apigment pickled with 30 wt. % HNO₃

the similar structure may be attributed to the presence of InVO₄ phase (Table 3). When the phase is removed from the pigment by means of pickling (samples marked with ^a), the value of the parameter *a*^{*} is reduced, *e.g.* from 11.10 to 8.50 for the sample P-2, or from 11.60 to 9.32 for the sample P-3. At the same time, the lightness of the pigments increases significantly: ΔL^* is 2.22 and 1.22, respectively.

On the grounds of comparable values of ionic radiuses of the ions of indium ($r_{In}^{3+} = 81 \text{ \AA}$) and zirconium ($r_{Zr}^{4+} = 80 \text{ \AA}$), a hypothesis has been put forward that the modifier ions are built into the ZrO₂ lattice, *e.g.*:



which, in consequence, changes the colour of the pigment from yellow-green to yellow-orange.

An X-ray microanalysis with the use of the EDX technique in randomly selected structure areas of the P-4 pigment identified a uniform distribution of the elements contained in the pigment. V₂O₅ concentration within the range of 0.34–0.40 wt. % was in good correspondence with the results of chemical analysis. The determined content of In₂O₃ was

Table 4. Results of EDX microanalysis of pigment P-4.

Chemical composition, wt. %	Spot measurements				
	1	2	3	4	5
ZrO ₂	95.04	95.06	95.47	96.36	96.09
V ₂ O ₅	0.40	0.38	0.40	0.39	0.34
In ₂ O ₃	1.85	1.89	1.40	1.38	1.85
TiO ₂	0.00	0.00	0.00	0.01	0.00
HfO ₂	1.79	1.75	1.75	1.77	1.70
Total	99.08	99.05	99.02	99.91	99.98

1.40–1.89 wt. % (Table 4), and the modifier quantity missing for the balance may be explained by its removing from the reaction environment due to intensive In₂O₃ sublimation in the synthesis conditions.

Modifying a zirconium-vanadium pigment (ZrO₂·V) with yttrium oxide produces, like in the case of In₂O₃, a change in its colour to yellow-orange but of lesser intensity. High chromaticity *C*_{ab}^{*}: 45.45–46.90 and lightness *L*^{*}: 77.99–75.75 is obtained in a narrow range of Y₂O₃ addition to the raw material batch: 1.0–2.0 wt. % (Table 5).

Table 5. Properties of pigments made on the basis of the raw material batch P-0 modified with yttrium oxide, fired at 1300 °C/1 h.

No	Properties	Pigment symbol					
		P-0	P-5	P-6		P-7	
1	Y ₂ O ₃ content in the raw material batch, wt. %	–	1.0	1.5		2.0	
2	Quantitative phase composition of the pigment washed with water, wt. %						
	– ZrO ₂ monoclinic:	92.3±0.7	93.3±0.6	93.4±0.5		93.0±0.6	
	– ZrV ₂ O ₇	4.5±0.4	1.6±0.3	b.d.		1.4±0.3	
	– V ₂ O ₅	1.5±0.1	2.7±0.4	b.d.		2.1±0.4	
	– NaV ₆ O ₁₅	1.6±0.6	–	b.d.		–	
	– YVO ₄	–	2.3±0.3	b.d.		3.5±0.3	
3	Vanadium content, [V, wt. %]:						
	– in a pigment washed with water,	2.30	2.32	2.50		2.69	
	– built into the structure	0.34	0.46	0.68		0.87	
4	Share of vanadium compounds in waste, after washing the pigment with water, [V, g/100 g of the pigment]	0.74	0.73	0.60		0.47	
5	Colour parameters of glazes:		<i>a</i>		<i>a</i>		
	– <i>L</i> *	80.67	75.75	77.99	76.02	77.17	76.38
	– <i>a</i> *	1.03	8.64	5.88	8.57	6.72	8.57
	– <i>b</i> *	44.39	45.91	46.53	45.21	44.99	44.64
	– <i>C</i> _{ab} *	44.40	46.49	46.90	46.90	45.59	45.45
	– Δ <i>E</i> *	–	9.19	5.94	8.90	6.70	8.68

^apigment pickled with 30 wt. % HNO₃

When the content of Y₂O₃ was higher than 2 wt. %, it had an adverse effect on the colour of the pigment: it reduced the chromaticity and increased the lightness [9]. A greenish colour of the pigment (*a** = –2.57), obtained at higher contents of Y₂O₃ comes most probably from a layer of vanadium pentoxide (V₂O₅) that is not built into the ZrO₂ lattice but is adsorbed on the surface of the pigment grains.

An X-ray analysis of phase composition of the pigments (Table 5) revealed, apart from the basic phase of ZrO₂, also vanadium-containing compounds: ZrV₂O₇, V₂O₅, NaV₆O₁₅, and in pigments modified with yttrium oxide – YVO₄ as well.

The analysis (Table 5) indicates that almost all the modifier was used for forming the YVO₄ phase. This means that the affinity of yttrium oxide to vanadium oxide is closer than to ZrO₂: yttrium is not built into the ZrO₂ lattice. Favourable conditions for

incorporating higher quantities of vanadium chromophore into the lattice are created with the increasing Y₂O₃ content in the raw material batch, which has a beneficial effect on improving the colour parameters of the pigments. Colour differences in comparison to an unmodified pigment reach: ΔE^* : 8.68–9.19, and 5.94–6.70 for pickled pigments (Table 5).

A conclusion may be drawn that in the course of a baddeleyite pigment synthesis the addition of Y₂O₃ has an advantageous effect on the quantity of vanadium built into the structure. The opinion diverges from the earlier published data on the role and occurrence of yttrium in the pigment structure [9, 20].

An addition of Y₂O₃ produces an effect of increased vanadium concentration in the pigment structure and, therefore, reduces by twofold the concentration of vanadium compounds in the technological waste (Table 5).

4. Conclusions

On the basis of analyses of the carried out tests it can be stated that:

1. Small additions of Y_2O_3 , In_2O_3 to the raw material batch increase the values of the parameters a^* and b^* as compared to unmodified pigments. New pigment varieties with yellow-orange colour are produced.
2. Modifying a pigment with indium oxide results in an increased share of red colour ($\Delta a^* = 10.57$). Yttrium oxide increases the value of yellow colour ($\Delta b^* = 2.14$). Both modifiers reduce the pigment lightness ($\Delta L^* = 4.92\text{--}6.89$).
3. The level of vanadium chromophore built into the ZrO_2 lattice, being 0.495 wt.% (V ions) for an unmodified pigment, was almost doubled as a result of using Y_2O_3 as a modifier. The remaining quantity of the chromophore material formed crystal phases containing vanadium in ZrV_2O_7 , V_2O_5 , $\text{NaV}_6\text{O}_{15}$, YVO_4 , InVO_4 , which had a beneficial effect on the pigment colour as it was demonstrated in the course of pickling with nitric acid.
4. Low content of Y_2O_3 (1–2 wt.%) revealed a mineralizing role of Y^{3+} ions as well as a possibility of substituting the ions of In^{3+} into the ZrO_2 structure instead of the “green” ions of vanadium in an oxidation state of +3.

References

- [1] BURGIAN A., *Interceram*, 28, 1 (1968), 30.
- [2] EVANS W.D.J., *Trans. Brit. Ceram. Soc.*, 67, 9 (1968), 397.
- [3] REGNIER R., *L'industrie Ceramique*, 1 (1971), 21.
- [4] RAY E.H., CARNAHAN T.D., SULLIVAN R.M., *Ceramic Bulletin*, 40, 1 (1961), 13.
- [5] BOOTH F.T., PEEL G.N., *Trans. Brit. Ceram. Soc.*, 61, 7 (1962), 258.
- [6] MATKOVICH V.I., CORBETT P.M., *J. Am. Ceram. Soc.*, 1 (1961), 128.
- [7] CZEREPANOV S.B., *Steklo i Keramika*, 22, 6 (1961), 8.
- [8] LAMBIES LAVILLA V., RINCON LOPEZ J.M., *Trans. J. Brit. Ceram. Soc.*, 3 (1981), 105.
- [9] DZIUBAK C., *Ceramika*, 66 (2001), 201.
- [10] REN F., ISHIDA S., TKEUCHI N., *J. Am. Ceram. Soc.*, 76, 7 (1993), 1825.
- [11] WEYL W.A., *Patentschrift Germany*, 1015 157 22, 22 octob. (1959).
- [12] DZIUBAK C., *Szkło i Ceramika*, 3 (2008), 4.
- [13] ŠOLC Z., TROJAN M., *Sklář a Keramik*, 39 (1989), 16.
- [14] TAYLOR J.R., *J. Bull. Ceram. Soc.*, 4, 2 (1967), 201.
- [15] EPPLER R.A., *Ceram. Bull.*, 56, 2 (1977), 213.
- [16] CLARENCE M., SEABRIGHT A., *Pat. France*, 1.281.456 (1960).
- [17] HUND F., GANTER K.W., *Pat.* 1 106 989 (1961).
- [18] MESIKOVÁ Ž., ŠULCOVÁ P., VÁLEK L., *Ceramika*, 96 (2006), 357.
- [19] DZIUBAK C., PIECZAROWSKI H., *Szkło i Ceramika*, 3–4 (1987), 85.
- [20] DZIUBAK C., *Ceramika*, 91 (2005), 905.

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