Research Article

Synthesis and Characterization of Rutile Pigments with Cr and Nb

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Rutile pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2+\delta}$ (where $x = 0, 0.05, 0.10, 0.20, 0.30$ and 0.50) prepared by solid-state reaction are investigated. Chromium is chromophore (coloring ion) and niobium is counterion (charge-compensating element for electroneutrality). The effect of composition (x), calcination temperature (850, 900, 950, 1000, 1050, 1100 and 1150°C), and starting titanium compounds (anatase TiO_2 , hydrated anatase paste, $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$, and hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste) on their color properties into organic matrix and particle size distribution was observed. According to the highest chroma C and visual color evaluation, yellow and orange pigments were selected as in color the most interesting. They have concentration $x = 0.05$ or 0.10 and are prepared from anatase TiO_2 and $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ at temperature $\geq 1050^\circ\text{C}$.

1. Introduction

The goal of this work was to evaluate the influence of composition ($x = 0, 0.05, 0.10, 0.20, 0.30$, and 0.50), calcination temperature (850, 900, 950, 1000, 1050, 1100, and 1150°C), and starting titanium compounds (anatase TiO_2 , hydrated anatase paste, $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$, and hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste) on color properties and particle size distribution of the rutile pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2+\delta}$ into organic matrix. Sb is the most widely used charge-compensating element for commercial rutile pigments, but it is ecologically problematic. This is the reason why we studied rutile pigments with Nb, which can also offer interesting pigments. Raw materials have an effect on properties of pigments as well; therefore, four various starting titanium compounds were used. In addition, selected pigments were analyzed by X-ray powder diffraction.

Rutile pigments are commercially manufactured pigments based on tetragonal mineral rutile (TiO_2) and they belong to the most important group of complex inorganic color pigments (CICPs) [1]. They are used for coloring ceramic glazes and porcelain enamels, plastics, inks, building materials, external paints, foods, and so forth [2, 3].

Solid solutions of chromium- (III) doped rutile have gained considerable recognition as durable, chemical resistant inorganic pigments with thermal stability over 1000°C [4]. The crystal structure of rutile pigments is modified by doping elements (chromophores and counterions), which vary the cell parameters [5].

In 1962, Hund issued a patent on the preparation of rutile pigments, which demonstrates the ability of rutile to form solid solutions with many compounds. Three fundamental rules were given for the formation of a rutile pigment. Firstly, substitutional atoms must have ionic sizes similar to Ti^{4+} (0.61 Å) or O^{2-} (1.40 Å). Secondly, charge balance (electroneutrality) should be maintained and, thirdly, the cation: anion ratio should remain at 1:2, as in TiO_2 . The last two rules require the use of at least two dopants for the commercial pigments [3, 6].

Industrial rutile pigments are manufactured using several chromophores (coloring ions) with oxidation state lower than 4+; for example, Ni^{2+} gives yellow hue, Mn^{2+} brown, Cr^{3+} from yellowish-brown to orange, and V^{3+} from grey to black. A second element (the so-called counterion, that is, Sb^{5+} , Nb^{5+} , Mo^{6+} , or W^{6+}) with oxidation state higher than 4+ is

TABLE 1: The mass composition of initial reaction mixtures for synthesis of pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$.

x	Cr_2O_3	Nb_2O_5	Anatase TiO_2	Mass (g)	$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$	Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste
0	—	—	30.00	34.49	73.61	38.59
0.05	1.35	4.71	24.08	27.69	59.08	30.97
0.10	2.55	8.93	18.78	21.60	46.09	24.16
0.20	4.62	16.16	9.71	11.16	23.82	12.49
0.30	6.33	22.13	2.22	2.55	5.44	2.85
0.50	7.55	26.62	—	—	—	—

always added in order to fulfill the electroneutrality of the structure. These elements occur in rutile pigments and also in other oxidation states, such as Ni^{3+} , Mn^{3+} , Cr^{4+} , V^{4+} , Sb^{3+} , Mo^{5+} , and W^{5+} [7].

Synthesis of these materials is based on solid-state reaction and uses Hedvall effect, that is, irreversible exothermic ($-12.6 \text{ kJ} \cdot \text{mol}^{-1}$) phase transformation from anatase modification of titanium dioxide to rutile. This transition takes place at temperature range 400 to 1200°C (it depends on many factors) but it most often takes place at temperature around 850°C , and it is related to the formation of highly defective reactive lattice, in which at the time of transformation it is possible to incorporate other ions [7–10].

2. Materials and Methods

2.1. Synthesis of Rutile Pigments. Suppliers and purities of raw materials are as follows: anatase TiO_2 (99 wt.%, Precheza, a.s. Přerov, CZ), hydrated anatase paste (87 wt.% TiO_2 , Precheza, a.s. Přerov, CZ), $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ (93 wt.%, Heubach, GmbH Langelsheim, DE), hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste (93 wt.%, Precheza, a.s. Přerov, CZ), Cr_2O_3 (99 wt.%, KOLTEX COLOR, s.r.o. Mnichovo Hradiště, CZ), and Nb_2O_5 (99.5 wt.%, Bochemie, a.s. Bohumín, CZ).

The mentioned starting compounds were chosen for synthesis of rutile pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$ (where $x = 0, 0.05, 0.10, 0.20, 0.30$, and 0.50) by solid-state reaction at calcination temperatures 850, 900, 950, 1000, 1050, 1100, and 1150°C . Mass of these raw materials was calculated for 30 g of final product (Table 1). Powdered raw materials were homogenized in a porcelain mortar; 4 g of reaction mixture was annealed in an electric furnace at all temperatures for 2 hours with heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ in air atmosphere. Prepared pigments were applied to organic matrix dispersive acrylic varnish Parketol (Balakom, a.s. Opava, CZ) in mass-tone by underdescribed method and particle size distribution with phase composition of selected pigments was also measured.

2.2. Measurement of Color Properties of Applied Rutile Pigments. Sample ($\sim 1 \text{ g}$) was pulverized in an agate mortar and binder ($\sim 1.5 \text{ cm}^3$) was added. This system was converted by a pestle to dense paste capable of flowing. Subsequently, created paste was dashed by a steel spatula on the glazed white nonabsorbing paper (with size $7 \times 8.5 \text{ cm}$) so that paste created a lengthwise “puddle” at the paper upper end. A plain layer of paint film was created by a pulling of the Bird (or

Wasag) film applicator with film width of $100 \mu\text{m}$ over the paste along the paper. Coating prepared by this way is ready for an evaluation of a color properties of the pigments into organic matrix in mass-tone after 1 to 2 hours spontaneous drying.

Spectrophotometer ColorQuest XE (HunterLab, Inc. Reston, USA) has wavelength range from 400 to 700 nm, wavelength interval 10 nm, and xenon lamp. Standard illuminant D65 is used like internationally recommended white daylight, measurement condition is $d/8^\circ$ and 10° supplementary standard observer and color space CIE $L^*a^*b^*$ are used. L^* is lightness from 0 (black) to 100 (white); a^* and b^* are color tones from $+a^*$ (red) to $-a^*$ (green) and from $+b^*$ (yellow) to $-b^*$ (blue). Chroma C and hue H^0 of color were calculated from (1). Chroma C determines a purity of color from 0 (grey) to 100 (pure color); it means that chroma is the degree of difference between a color and grey. Hue H^0 has interval 0 to 360° and for red color it has value $350\text{--}35^\circ$, for orange $35\text{--}70^\circ$, for yellow $70\text{--}105^\circ$, for green $105\text{--}195^\circ$, for blue $195\text{--}285^\circ$, and for violet $285\text{--}350^\circ$ [11]:

$$C = (a^{*2} + b^{*2})^{1/2},$$

$$H^0 = \arctg \left(\frac{b^*}{a^*} \right). \quad (1)$$

2.3. Measurement of Particle Size Distribution of Rutile Pigments. Laser apparatus Mastersizer 2000/MU (Malvern Instruments, Ltd. Worcestershire, UK), which uses the laser diffraction on particles dispersed in some medium and which enables assessing measured signal by Mie scattering theory and Fraunhofer diffraction theory, was used for measuring of particle size distribution. Its wide size range is from 20 nm to 2 mm. A blue light (wavelength 466 nm, solid-state light source) for wide angle forward and back scattering is used in conjunction with red light (wavelength 633 nm, He-Ne laser) for forward, side, and back scattering.

At measuring, solution $\text{Na}_4\text{P}_2\text{O}_7$ (40 mL, $0.15 \text{ g} \cdot \text{L}^{-1}$) was added to the sample (0.5 g) crushed in agate mortar. This suspension was dispersed in ultrasonic bath for 2 minutes. During dispergation, solution $\text{Na}_4\text{P}_2\text{O}_7$ (4.8 mL , $3 \text{ g} \cdot \text{L}^{-1}$) was added to distilled water (800 mL) and background was measured. Dispersed suspension was poured into this solution immediately after dispergation up to maximum concentration of $12.5 \pm 0.5\%$ and measuring was turned on. The measurement of particle size distribution has three

TABLE 2: An effect of composition on color properties of pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$ prepared at calcination temperature 1050°C.

x	Anatase TiO_2					Hydrated anatase paste				
	L^*	a^*	b^*	C	$H^0 (^\circ)$	L^*	a^*	b^*	C	$H^0 (^\circ)$
0	93.49	-0.64	4.16	4.21	98.75	92.17	-1.36	9.90	9.99	97.82
0.05	64.05	17.26	41.84	45.26	67.58	52.55	6.87	22.94	23.95	73.33
0.10	59.14	17.12	39.25	42.82	66.43	51.92	7.14	24.99	25.99	74.05
0.20	52.29	13.79	33.75	36.46	67.78	49.22	7.68	24.62	25.79	72.68
0.30	44.56	8.35	25.17	26.52	71.65	47.20	7.77	22.22	23.54	70.73
0.50	44.88	6.73	22.01	23.02	73.00	44.88	6.73	22.01	23.02	73.00

x	$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$					Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste				
	L^*	a^*	b^*	C	$H^0 (^\circ)$	L^*	a^*	b^*	C	$H^0 (^\circ)$
0	92.42	-0.42	4.81	4.83	94.99	94.27	0.64	2.05	2.15	72.66
0.05	71.26	12.33	41.51	43.30	73.46	68.82	3.32	35.20	35.36	84.61
0.10	64.01	15.51	40.32	43.20	68.96	58.30	5.18	36.55	36.92	81.93
0.20	56.89	11.06	33.08	34.88	71.51	48.59	8.18	22.70	24.13	70.18
0.30	48.20	6.32	25.48	26.25	76.07	47.72	7.97	24.45	25.72	71.95
0.50	44.88	6.73	22.01	23.02	73.00	44.88	6.73	22.01	23.02	73.00

steps and instrument calculates the average automatically like values d_{10} , d_{50} , and d_{90} .

2.4. X-Ray Powder Diffraction of Rutile Pigments. Phase composition of some pigments was determined by diffractometer D8 Advance (Bruker AXS, Ltd. Coventry, UK) equipped with a vertical θ - θ goniometer (radius 217.5 mm). X-ray tube with Cu anode ($U = 40$ kV, $I = 30$ mA), secondary graphite monochromator, scintillation NaI (TI) counter, and X-ray of copper are used. Wavelength of applied X-ray is $K_\alpha = 0.15418$ nm. Measuring range of 2θ is from 10 to 80° with a step 0.02° and step time 3 s at 25°C .

3. Results and Discussion

3.1. Color Properties (L^* , a^* , b^* , C and H^0) of Applied Rutile Pigments. The color of rutile pigments appears to develop contemporarily to the anatase to rutile transformation and the solid solution of chromophores and counterions into the rutile structure, though some sequential order is claimed in the literature [3]. These reactions are probably associated with valence changes of some cations [3, 5, 7, 12, 13]. As a matter of fact, the color evolves along with the amount of rutile; nevertheless, this change in hue and chroma goes beyond the total transformation of anatase in rutile, confirming analogous experimental observations [14].

Color properties of rutile pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$ were studied depending on composition ($x = 0, 0.05, 0.10, 0.20, 0.30$, and 0.50), calcination temperature (850, 900, 950, 1000, 1050, 1100, and 1150°C), and starting compounds of titanium (anatase TiO_2 , hydrated anatase paste, $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$, and hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste).

3.1.1. An Effect of Composition on Color Properties of Pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$. It is possible to determine, from Table 2, that in all cases (for all starting titanium compounds)

lightness L^* decreases (overall from 94 to 45) as the dopant contents (x) increased, so pigments darken. Next, for anatase TiO_2 like raw material, the color coordinates a^* , b^* , chroma C , and hue H^0 also decrease and pigments are orange to brown. The dependences of color coordinates of pigments prepared from other starting titanium compounds on the amount of doping elements are mostly more complicated. Color coordinates of pigments obtained from hydrated anatase paste increase to $x = 0.10$ (for b^* and C) or 0.30 (for a^*) and after that they decrease. At $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ like raw material, a^* grows to $x = 0.10$ and b^* and C decline. Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste gives rutile pigments, whose color magnitude a^* rises to $x = 0.2$ and b^* and C vary differently. According to the highest chroma C and visual color evaluation, the more saturated and purer colors are developed at concentration of doping elements $x = 0.05$ and 0.10 . The color of these pigments is yellow, orange, and green (Table 7), chroma $C = 24$ – 45 , and red hue a^* is mostly higher than for other concentrations.

The decline of lightness L^* with growing concentration of dopants is expected, because pure (undoped) rutile is white and has lightness almost 100. So, doping elements cause the decrease of L^* , which according to its definition cannot be higher than 100.

Color hue H^0 has overall interval 66 to 99° , which corresponds to yellow, orange, and greenish colors. However, some pigments are brown. It is caused by low values of lightness L^* at higher concentrations. In addition, hue H^0 is calculated from values a^* and b^* only and does not include the lightness L^* . The pigments with the highest chroma C (24 – 45) are characterized by hue H^0 in the range of 66 – 85° .

3.1.2. An Effect of Calcination Temperature on Color Properties of Pigments $\text{Ti}_{0.85}\text{Cr}_{0.05}\text{Nb}_{0.10}\text{O}_{2\pm\delta}$ ($x = 0.05$). This effect is summarized in Table 3. Generally, lightness L^* mainly decreases (from 76 to 51) with calcination temperature. Red

TABLE 3: An effect of calcination temperature on color properties of pigments $\text{Ti}_{0.85}\text{Cr}_{0.05}\text{Nb}_{0.10}\text{O}_{2\pm\delta}$.

$T (^{\circ}\text{C})$	Anatase TiO_2					Hydrated anatase paste				
	L^*	a^*	b^*	C	$H^0 (^{\circ})$	L^*	a^*	b^*	C	$H^0 (^{\circ})$
850	75.67	-2.63	15.84	16.06	99.43	75.56	-1.61	21.22	21.28	94.34
900	77.66	0.62	17.27	17.28	87.94	73.71	0.55	22.74	22.75	88.61
950	69.36	3.04	19.80	20.03	81.27	67.21	3.07	21.47	21.69	81.86
1000	59.48	7.21	27.88	28.80	75.50	50.57	6.23	19.46	20.43	72.25
1050	64.05	17.26	41.84	45.26	67.58	52.55	6.87	22.94	23.95	73.33
1100	60.40	21.74	43.18	48.34	63.28	52.15	11.99	28.18	30.62	66.95
1150	58.32	23.89	43.91	49.99	61.45	50.76	10.81	24.48	26.76	66.17

$T (^{\circ}\text{C})$	$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$					Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste				
	L^*	a^*	b^*	C	$H^0 (^{\circ})$	L^*	a^*	b^*	C	$H^0 (^{\circ})$
850	73.36	1.17	25.79	25.82	87.40	72.84	2.06	38.94	38.99	86.97
900	77.26	3.56	35.90	36.08	84.34	72.29	2.02	37.59	37.64	86.92
950	75.40	5.32	37.78	38.15	81.98	69.85	1.75	35.21	35.25	87.15
1000	72.98	7.77	39.20	39.96	78.79	68.62	2.96	35.23	35.35	85.20
1050	71.26	12.33	41.51	43.30	73.46	68.82	3.32	35.20	35.36	84.61
1100	71.23	12.24	41.43	43.20	73.54	63.27	4.18	31.48	31.76	82.44
1150	67.70	14.77	41.06	43.64	70.22	58.26	1.50	29.16	29.20	87.06

tone a^* grows (from -3 to 24) except pigments prepared from hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste, where it changes variously (2–4). Yellow tone b^* and chroma (purity) C increase excepting compounds obtained from hydrated anatase paste (variation) and hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste (decline). The optimal calcination temperature for synthesis of this type of pigments is 1050°C and higher, because of their great chroma C (24 to 50) and interesting colors. These materials are yellow, orange, and green (Table 8). However, compounds synthesized from hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ are the most saturated at lower calcination temperatures.

In most cases, color hue H^0 decreases with temperature. Yellow, orange, and green colors result from values of H^0 , which are 62 to 99°. The calcination temperature almost does not influence pigments prepared from hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste.

3.1.3. An Effect of Starting Titanium Compounds on Color Properties of Pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$. The color of prepared rutile pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$ into organic matrix is yellow, orange, brown, and green according to the synthesis conditions. This is shown in Tables 7 and 8. $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ provides in color the most different pigments. Single color coordinates lie in intervals $L^* = 45\text{--}94$, $a^* = -3\text{--}24$, $b^* = 4\text{--}44$, $C = 2\text{--}50$, and $H^0 = 62\text{--}99^\circ$. From measured data it is clearly established that the final quality of the pigments strongly depends on all these parameters (concentration of doping elements, calcination temperature, and starting titanium compounds). Positive values of a^* and b^* were obtained almost for all samples and mean green, yellow, and orange hues of pigments. Brown color is caused by lower values of lightness L^* .

It is clear from measured data that color coordinates of pigments prepared from hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste are markedly different. It is most probably caused by sodium,

which acts as a mineralizer and affects a course of the solid-state reaction favorably. Sodium can also act as a deoxidizer or can control the growth of pigmentary particle or can improve reaction between raw materials [3].

At the temperature 1050°C, the color coordinates of prepared pigments are mostly similar. However, it is possible to find out, from numeric values, that the mentioned pigments obtained from hydrated anatase paste give the darkest tones (the lowest lightness L^*) with the lowest chroma (purity) C . On the contrary, chroma reaches the highest values for pigments synthesized from anatase TiO_2 and $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$. The color of materials is similar (brown) at higher concentration of doping elements ($x = 0.20\text{--}0.50$) with H^0 over 70° and L^* below 50, but, for lower x , the hue is yellow, orange, and green, whereas the H^0 has interval from 66 to 85° and L^* from 52 to 71.

In respect of composition ($x = 0.05$), the color coordinates are very different depending on starting titanium compounds. Pigments that originated in hydrated anatase paste are the darkest and the least saturated again. It is the same for pigments prepared from anatase TiO_2 and $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$, which have the highest chroma. $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ gives yellow and hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste gives green pigments mostly.

3.2. Particle Size Distribution of Rutile Pigments. According to the values in Tables 4 and 5, the growing concentration of doping elements and also calcination temperature result in the increasing of mean particle size d_{50} . This is why the pigments darken. This particle size is the smallest for pigments prepared from $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ (0.9–5.5 μm) and the biggest for materials obtained from hydrated anatase paste (1.3–7.3 μm).

The optimal particle size of pigments for glaze applications is from 5 to 15 μm . But prepared pigments have

TABLE 4: An effect of composition on particle size distribution of pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$ prepared at calcination temperature 1050°C .

x	Anatase TiO_2			Hydrated anatase paste		
	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$
0	1.01	8.47	34.87	0.70	1.44	3.64
0.05	0.74	2.04	24.49	1.07	2.77	33.27
0.10	0.78	2.44	24.80	1.08	3.27	31.03
0.20	0.75	3.98	26.29	1.00	3.83	23.81
0.30	1.00	6.03	28.28	1.31	7.26	71.12
0.50	1.28	7.03	29.93	1.28	7.03	29.93

x	$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$			Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste		
	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$
0	0.36	1.04	24.13	0.51	2.79	28.59
0.05	0.60	1.32	14.17	0.52	1.41	7.36
0.10	0.67	1.75	20.34	0.73	1.91	9.77
0.20	0.75	2.42	24.97	0.85	2.53	19.09
0.30	1.01	5.52	30.90	0.60	2.33	16.58
0.50	1.28	7.03	29.93	1.28	7.03	29.93

TABLE 5: An effect of calcination temperature on particle size distribution of pigments $\text{Ti}_{0.85}\text{Cr}_{0.05}\text{Nb}_{0.10}\text{O}_{2\pm\delta}$.

$T (^\circ\text{C})$	Anatase TiO_2			Hydrated anatase paste		
	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$
850	0.28	0.81	17.37	0.48	1.33	14.86
900	0.30	0.84	21.58	0.51	1.47	25.19
950	0.35	0.95	19.91	0.54	1.63	24.50
1000	0.69	2.03	26.50	0.90	2.42	25.19
1050	0.74	2.04	24.49	1.07	2.77	33.27
1100	0.82	2.48	25.66	1.38	3.17	8.78
1150	0.88	3.14	30.14	1.46	3.37	11.81

$T (^\circ\text{C})$	$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$			Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste		
	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$	$d_{10} (\mu\text{m})$	$d_{50} (\mu\text{m})$	$d_{90} (\mu\text{m})$
850	0.36	0.85	12.47	0.53	2.95	26.54
900	0.42	1.05	28.99	0.60	3.00	24.66
950	0.43	1.17	30.14	0.45	1.73	22.36
1000	0.48	1.09	8.73	0.51	1.46	21.38
1050	0.60	1.32	14.17	0.52	1.41	7.36
1100	0.61	1.35	16.31	0.57	1.64	12.12
1150	0.87	2.34	31.28	1.03	6.18	36.55

particles mostly below this interval and therefore the results of these applications are not so good (because of their partial solubility into the glazes over 1000°C). This drawback can be minimized using special Ti-rich glazes that unfortunately exhibit both technological (high thermal expansion coefficient) and aesthetic (high refractive index and strong brilliance) limitations [7]. Other two possibilities can be proposed: firstly, using of relative high size of pigmentary particles which produce a coarse coloration and, secondly, using of *in situ* synthesis of pigment during glazing (for 1 hour at maximum temperature 1200°C and with 5-minute soaking). For these self-generating pigments, it is necessary to use raw materials, which in glazes form the pigments during glazing and do not react with glaze [15].

3.3. The Results of X-Ray Powder Diffraction of Rutile Pigments. All prepared compounds have crystalline character and they are single-phase to four-phase (Table 6, Figure 1). The phase composition of pigments prepared from anatase TiO_2 , hydrated anatase paste, and $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ is similar and characterized by peaks corresponding to almost pure rutile phase, but with Nb_2O_5 , CrNbO_4 , and $\text{Ti}_{0.93}\text{Cr}_{0.07}\text{O}_{1.965}$ for hydrated anatase paste. Only phase composition of materials obtained from hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste is very different (rutile, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, NaNbO_3 , and $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$) because of sodium, which is incorporated to the structure of compounds in the form of titanates and niobates. Probably, it is the reason why the color of these compounds and the trends in the changes of their color coordinates are different

FIGURE 1: The results of X-ray powder diffraction of pigments $\text{Ti}_{0.85}\text{Cr}_{0.05}\text{Nb}_{0.10}\text{O}_{2\pm\delta}$ prepared from anatase TiO_2 , hydrated anatase paste, $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$, and hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste at calcination temperature 1050°C .

from the other starting titanium compounds. In addition, the intensity of peaks for hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste is very small in comparison with other titanium raw materials.

The peaks are the sharpest and the most intense for $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ (indicating improved crystallization); then those for hydrated anatase paste and anatase TiO_2 follow, respectively. Even if the pigments obtained from these raw materials have near phase composition, their colors are various. It is clearly established that the higher number of phases into the structure results in lower values of chroma (purity) C of color (viz hydrated anatase and $\text{Na}_2\text{Ti}_4\text{O}_9$ paste). In comparison to the diffraction patterns of selected

pigments, lines shifted towards smaller angles correspond to bigger values of interplanar distance d in the following order: anatase TiO_2 < hydrated anatase paste < $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ < hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste.

4. Conclusions

During this research, rutile pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$ (where $x = 0, 0.05, 0.10, 0.20, 0.30$, and 0.50) were synthesized by classical ceramic method at firing temperatures $850, 900, 950, 1000, 1050, 1100$, and 1150°C from four various starting titanium compounds (anatase TiO_2 , hydrated anatase paste,

TABLE 6: An effect of starting titanium compounds on phase composition of pigments $\text{Ti}_{0.85}\text{Cr}_{0.05}\text{Nb}_{0.10}\text{O}_{2\pm\delta}$ prepared at calcination temperature 1050°C [16].

	Phase composition	Crystal system	JPDF number
Anatase TiO_2	Rutile TiO_2	Tetragonal	04-003-0648
	Rutile TiO_2	Tetragonal	04-003-0648
Hydrated anatase paste	Nb_2O_5	Monoclinic	00-037-1468
	CrNbO_4	Tetragonal (rutile)	00-034-0366
	$\text{Ti}_{0.93}\text{Cr}_{0.07}\text{O}_{1.965}$	Tetragonal (rutile)	04-015-2316
$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$	Rutile TiO_2	Tetragonal	04-003-0648
Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste	Rutile TiO_2	Tetragonal	04-003-0648
	$\text{Na}_2\text{Ti}_6\text{O}_{13}$	Monoclinic	04-009-8328
	NaNbO_3	Orthorhombic	04-009-6249
	$\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$	Monoclinic	00-052-1309

TABLE 7: Color card of pigments prepared at calcination temperature 1050°C and applied to organic matrix in mass-tone with influence of composition.

x	0	0.05	0.10	0.20	0.30	0.50
Anatase TiO_2						
Hydrated anatase paste						
$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$						
Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste						

TABLE 8: Color card of pigments $\text{Ti}_{0.85}\text{Cr}_{0.05}\text{Nb}_{0.10}\text{O}_{2\pm\delta}$ applied to organic matrix in mass-tone with influence of calcination temperature.

T (°C)	850	900	950	1000	1050	1100	1150
Anatase TiO_2							
Hydrated anatase paste							
$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$							
Hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste							

$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$, and hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ paste). The effect of these parameters on their color properties into organic matrix and particle size distribution was observed.

It was found that lightness L^* decreases with growing dopants concentration and calcination temperature, so pigments darken. According to the highest chroma C and visual color evaluation, the optimal conditions for synthesis of the mentioned pigments are concentration of doping

elements $x = 0.05$ and 0.10 and calcination temperature 1050°C and higher. However, compounds synthesized from hydrated $\text{Na}_2\text{Ti}_4\text{O}_9$ are the most saturated at lower calcination temperatures. The color of prepared rutile pigments $\text{Ti}_{1-3x}\text{Cr}_x\text{Nb}_{2x}\text{O}_{2\pm\delta}$ into organic matrix is yellow, orange, brown, and green and strongly depends on concentration of doping elements, calcination temperature, and starting titanium compounds.

Combination Ti-Cr-Nb proves suitable for rutile pigments with yellow ($\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$) and orange (anatase TiO_2) hues. Nb shows itself like dopant acceptable for this type of pigments and can replace the Sb because of its ecological disturbances.

It is evident from measured data that properties of rutile pigments do not depend only on dopants concentration and calcination temperature but also to a large extent on starting compounds, which afford new possibilities of research.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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