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YELLOW PIGMENTS BASED ON Fe_2TiO_5 AND TiO_2

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The aim of our research was to prepare yellow pigments based on structure of pseudobrookite Fe_2TiO_5. Part of Fe was substituted with Li and Ti from Fe_2TiO_5 to $Li_{0.05}Fe_{0.07}Ti_{2.44}O_5$. Synthesis and pigmentary-application properties in the Li_2O–Fe_2O_3–TiO_2 system were studied for 800 and 900°C using classical ceramic method of preparation. The main attention was aimed to usage of four different sources of titanium compounds as raw materials. We studied the influence of different sources of titanium compounds on the structural and the colour properties of the prepared pigments. The thermal analysis was used for characterization of titanium compounds and determination of their thermal stability.

Keywords: *pseudobrookites, thermal analysis, titanium dioxide, yellow-ochre pigments*

Introduction

Pseudobrookites belong to the group of titanate pigments. Pseudobrookite has a general formula Fe_2TiO_5. The challenge in making high-quality pseudobrookite pigments is obtaining complete reaction of Fe_2O_3. This is difficult reaction to force despite the availability on fine size pigmentary grades of Fe_2O_3 and TiO_2 for use as raw materials. Unfortunately, Fe_2O_3 can be found in XRD spectra of most commercial pigments, and is surely present in significant amounts even when it is undetectable in XRD patterns. One way how to prepare pseudobrookite pigments without presence of Fe_2O_3 in product is usage of a large excess of TiO_2 to help force complete reaction of Fe_2O_3. It leads in a rutile secondary phase that is sometimes dominant phase in the product [1]. Phase relations in the Li_2O–Fe_2O_3–TiO_2 system for 800 and 900°C were reported by Yau and Hughes [2]. Grey *et al*. [3] studied this system for temperature 1000°C. They characterized the extensive solid solutions based on the pseudobrookite-type and ramsdellite-type structures. Two three-phase fields were characterized, comprising ramsdellite+spinel+pseudobrookite and ramsdellite+pseudobrookite+rutile [3]. Pseudo-ternary compounds of $LiO_{0.5}$–X–TiO_2 (X=$FeO_{1.5}$, $CrO_{1.5}$ and NiO) system were prepared by Fujimoto using a fully automatic combinatorial robot with following functions: weighing and mixing of starting materials, heat treatment and X-ray diffraction analysis. The following crystal structures were obtained by means of heat treatment at 1373 K: ramsdellite, spinel, pseudobrookite, rock salt, hematite and rutile [4]. The systems Fe_2O_3/TiO_2 prepared by sol–gel method is also used like photocatalytic materials [5]. The results reported in this paper are part of our systematic investigation of new inorganic compounds that can be used as the pigments [6]. The compounds obtained as an intermediate product in the sulphate method of obtaining titanium dioxide can be used as precursors for preparation of other new inorganic pigments based on TiO_2. Therefore these intermediate products are objects of intensive investigations [7–10].

Experimental

All the samples were prepared by classical ceramic method. The main attention was aimed to usage of four different sources of titanium compounds as starting materials. We wanted to find out how different sources of titanium compound can affect the structural and the colour properties of the prepared pigment. The titanium compounds used for synthesis: $TiOSO_4{\cdot}nH_2O$ (Heubach GmbH, Germany), $Na_2Ti_4O_9$ paste (Precheza a.s. Přerov, Czech Republic) and TiO_2 in two different types of pastes – rutile paste and anatase paste (Precheza a.s. Přerov, Czech Republic). These pastes are water slurry of unaccommodating TiO_2.

The starting materials were homogenized in an agate mortar. The pastes were dried before homogenization. Then the mixtures were calcinated in corundum crucibles in an electric furnace with increasing of temperature 10°C min^{-1} and the temperature was maintained for one hour. After that the fired samples were decanted in hot water, filtrated and dried.

The thermal analysis was used for characterization of the starting materials of titanium. Measuring was carried out by means of STA Jupiter 449 equip-

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ment (Netzsch, Germany) in temperature interval 50–1200°C with increasing of temperature 10°C min^{-1}. The analysis was accomplished in ceramic crucible in air and α-Al_2O_3 was used as a reference material.

The structure of the powder samples were studied by X-ray diffraction analysis. The X-ray diffractograms of the samples in the range 10–80 2θ were obtained by measuring on an equipment diffractometer D8 (Bruker, GB), CuK_α radiation, scintillation detector.

Prepared pigments were compared based on colour properties after their application into organic matrix. Colour properties have been measured in the visible region of light (400–700 nm) with MiniScan MS/S (Hunter Lab, USA). The measurement conditions were following: illuminant D65 (6500 K), 10° complementary observer and geometry of measurements *d*/8°, colour space CIE $L^*a^*b^*$ and chroma *C*.

Results and discussion

TG and DTA curves of anatase paste of TiO_2 are plotted in Fig. 1. Total mass defect that is around 15% is caused by loss of water and by decomposition of residual sulphuric acid (Table 1). The first endothermic peak (146°C) is connected with the loss of crystalline water. The first stage of desulfuration runs at the temperature region 250–500°C. The endothermic effect with minimum at 574°C corresponds to decomposition of residual of sulphates. Next exothermic effect on DTA curve (861°C) indicates the transformation of anatase to rutile and at the same time this effect corresponds to the second stage of desulfuration (5.17%). The last effect that was identified on DTA curve at temperature 1058°C corresponds to the partial loss of oxygen connected with formation of lower oxides.

Table 1 Thermal decomposition of the TiO_2 anatase paste (Fig. 1)

Temperature range/°C	Peak temperature/°C	Mass loss/%
30–250	146	7.11
250–500	574	2.79
500–900	861	5.17

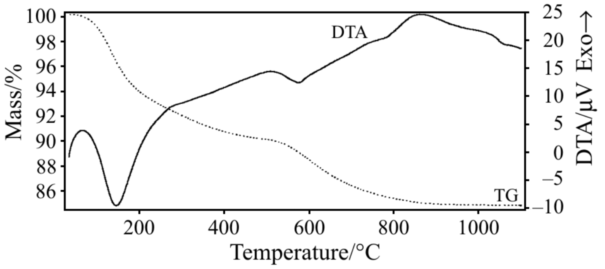

Fig. 1 TG and DTA curves of TiO_2, anatase paste (mass: 222.15 mg)

TG and DTA curves of the TiO_2 rutile paste are plotted at Fig. 2. Range of temperature 30–280°C is connected with the most mass loss 48.28% (Table 2). This is caused by loss of moisture, crystalline water and partial decomposition of sulphuric acid. The endothermic peak (573°C) is connected with decomposition of sulphate residual. The effect at temperature 1059°C corresponds again to the partial loss of oxygen connected with formation of lower oxides.

Table 2 Thermal decomposition of the TiO_2 rutile paste (Fig. 2)

Temperature range/°C	Peak temperature/°C	Mass loss/%
30–280	132 161	48.28
280–800	573	4.46

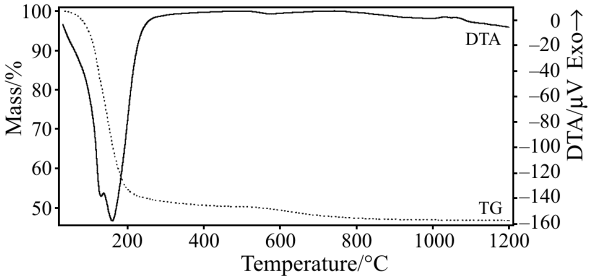

Fig. 2 TG and DTA curves of TiO_2, rutile paste (mass: 252.20 mg)

The next used titanium compound was $TiOSO_4{\cdot}nH_2O$. On DTA and TG curves of this compound there were identified two endothermic effects in range of temperature 50–290°C that correspond to loss of crystalline water (16.59%). The effect that indicates decomposition of sulphate was also identified on TG and DTA records.

The last titanium compound that was used for preparation of pseudobrookites was $Na_2Ti_4O_9$. The first endothermic effect with minimum at 156°C is caused by loss of water (12.75%). The next effect on DTA curve was identified at temperature region 400–500°C. This effect again corresponds to the decomposition of suphate residual, especially the first step of desulfuration. The process of desulfuration is finished at temperature region 500–900°C, the mass defect is 5.56% (Table 3, Fig. 3). The slight exothermal effect on DTA curve is associated with the formation of lower oxides (1024°C).

Two and three phases were identified by X-ray diffraction analysis of samples that were prepared by firing at temperature 800°C. Samples prepared from $TiOSO_4$ contained only two phases. Unexpectedly it was only rutile and anatase phase of TiO_2; pseudobrookite phase was not identified on X-ray pattern.

Table 3 Thermal decomposition of the paste $Na_2Ti_4O_9$ (Fig. 3)

Temperature range/°C	Peak temperature/°C	Mass loss/%
30–400	156	10.90
400–500	–	1.65
500–900	571	5.56

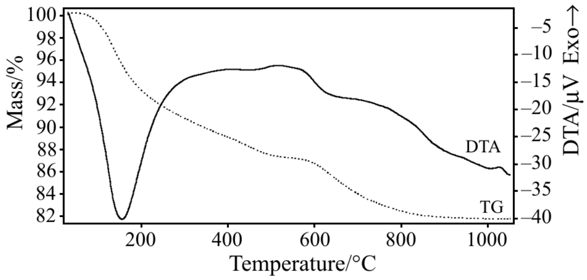

Fig. 3 TG and DTA curves of paste $Na_2Ti_4O_9$ (mass: 217.80 mg)

On the other patterns there were identified phases of rutile, anatase and pseudobrookite. The increase of temperature by 100°C brings formation of two-phased systems – pseudobrookite and rutile; in the case of $TiOSO_4$ precursor only one phase system (rutile) was created.

Prepared pigments have dark yellow to ochre colour. Colour of the pigments were measured in the visible region of light (400–700 nm) and results are resumed in Table 4. Generally, pigments prepared by firing at temperature 800°C are darker. They have lower values of colour coordinate L^* that express the extent of brightness. The pigment prepared from $Na_2Ti_4O_9$ is the lightest and has the highest value of brightness. Values of coordinates a^* that express the extent of red hue in this case are comparable. Considerable difference is betweeen values of coordinates b^* that express the extend of yellow hue. The pigment prepared from $Na_2Ti_4O_9$ contains the highest amount of yellow hue therefore it has also the highest value of chroma. The increase of temperature by 100°C makes pigments lighter. Values of coordinates a^* for pigments prepared from anatase and rutile pastes are slightly higher but values of coordinates b^* of all the samples significantly increased. The pigments prepared by firing at temperature 900°C has also higher chroma than pigments fired at 800°C. The most interesting ochre colour has pigment prepared from $Na_2Ti_4O_9$.

Table 4 Colour properties of the pigments $Li_{0.05}Fe_{0.07}Ti_{2.44}O_5$

T/°C	Titanium compound	L^*	a^*	b^*	C
800	anatase paste	75.79	10.90	15.93	19.30
	rutile paste	75.69	10.82	20.84	23.48
	$TiOSO_4{\cdot}nH_2O$	77.86	9.37	19.34	21.49
	$Na_2Ti_4O_9$	79.09	10.72	27.79	29.79
900	anatase paste	73.38	13.55	28.95	31.96
	rutile paste	76.06	11.80	26.96	29.43
	$TiOSO_4{\cdot}nH_2O$	78.56	10.16	25.10	27.08
	$Na_2Ti_4O_9$	81.15	10.30	32.33	33.93

Conclusions

The main aim of this research was to prepare ecological friendly inorganic compounds with good pigmentary properties that can be used as the pigments. The main attention was aimed to using of four different sources of titanium compounds as starting materials. The pigments prepared from $Na_2Ti_4O_9$ precursor and fired at temperature 900°C give the most interesting dark yellow to ochre colour properties. Generally, the temperature 900°C can be recommended for the preparation of compounds based on system Li_2O–Fe_2O_3–TiO_2 by classical ceramic method. Compounds prepared by firing at this temperature are two-phased and contain phases of pseudobrookite and rutile.

Acknowledgements

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