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COLOR CHARACTERISTICS OF ZIRCON PIGMENTS SYNTHESIZED FROM AGRICULTURAL WASTE

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ABSTRACT

The aim of the present paper is to study the possibilities to synthesize zirconium ceramic pigments from pure and waste materials with respect to their possible use as pigments in the silicate industry. Zircon pigments with main phase $ZrSiO_4$ are synthesized by heating a mixture of ZrO_2, SiO_2, chromophore ion and mineralizer. The raw materials for the synthesis of pigments are ZrO_2, Fe_2O_3, NH_4VO_3, Co_3O_4, Cr_2O_3, MnO_2, ash from rice husk as a source of SiO_2, and NH_4Cl as a mineralizer. The following elements have been added as colorants (chromophores): V, Fe, Cr, Co and Mn. The optimal parameters of synthesis are determined and the color characteristics of the synthesized zirconium ceramic pigments are measured with the CIELab system of color measurement.

Key words: *zircon pigments, rice husk, solid-state sintering, CIELab color measurement*

INTRODUCTION

In recent years the synthesis of new kinds of ceramic pigments has been based on the growing importance of ceramic materials, powders and pigments, as well as the diverse possibilities for obtaining them from both traditional and waste materials, as well as their potentially wide practical use in the ceramic and glass industries, e.g. coloring of ceramic tiles and other articles, mosaic tiles, coloring of glass to obtain various types of colored glasses, etc. Their color palette constantly increases with respect to the production of over-glaze paints and coloring of glazes for the ceramic industry, e.g. for tile production [1].

A number of researchers [2-3] focused their efforts on the mechanism of formation of zircon pigments, the role of the mineralizers, as well as the possibility to use various raw materials in the process. The selenites of the rare earth elements turned out to be quite suitable for the synthesis of zircon pigments.

Rice husks, which are an agricultural waste product, contain high percentage of SiO_2. The presence of a high content of silica in rice husk ash has been known since 1938, and extensive literature studies have highlighted the high use of ash as a substitute for pure silica [4].

Various studies have shown the effectiveness of using rice husks as a precursor to silica, especially for the production of ceramic materials. Prasad et al. [5] studied the effect of quartz replacement in ceramic vessels and found that silicon dioxide from the rice husk leads to a decrease in ripening temperature and an increase in strength.

Andreola et al. [4, 6] have investigated the use of silicon dioxide from rice husks for the synthesis of ceramic pigments. They have found more stable pigments and a higher intensity of red color compared to pure quartz pigments, while Sobrosa et al. [7] have reported that glass-ceramics produced with silica from rice husks has higher values of flexural strength and higher Mohs hardness in comparison with commercial glass-ceramics.

The aim of the present work is to synthesize zirconium ceramic pigments from pure and waste materials and study the possibilities for their application in the silicate industry.

EXPERIMENT

Methods

The zircon ceramic pigments were studied mainly by infrared spectroscopy (FT-IR) as well as with the CIELab system of color measurement.

Color Measurement. The color determination of the pigments is carried out spectrally with a tintometer of Lovibond Tintometer RT 100 Color.

The FT-IR studies were performed on a Tensor 27 Fourier infrared spectrophotometer FTIR (Bruker, Germany) in the 400 – 4000 cm^{-1} interval at a resolution of 1 cm^{-1}. The measurements were carried out at room temperature. The sample (0.3 mg) was tableted with KBr (100 mg) at a pressure of 2-4 atm. The DTA experiments were performed on an apparatus for complex thermal analysis (STA 449F3 Jupiter), NETZSCH, Germany by heating to 1100°C at a rate of 10°C min^{-1}.

Materials

Zircon pigments with a main crystalline phase zircon $ZrO_2.SiO_2$ were prepared by the solid phase sintering method. Both pure and waste raw materials were used as raw materials. The basic materials for the synthesis of zircon pigments were very finely ground chemically pure chemicals and waste raw materials. Pure ZrO_2 was used as the source of ZrO_2, and ash from oxidized rice husk was used as the source of SiO_2. The following elements were added as chromophores: V, Fe, Cr, Co and Mn. For this purpose, the following raw materials were used: Fe_2O_3, NH_4VO_3, Co_3O_4, Cr_2O_3 and MnO_2. The mineralizer used was NH_4Cl. The mineralizers play an important role in decreasing the temperature of the process. The compositions are presented in Table 1.

Table 1. Composition of the samples

№ of sample	ZrO_2	RHA	NH_4Cl	Fe	V	Co	Cr	Mn
ZR1	+	+	+	+				
ZR2	+	+	+		+			
ZR3	+	+	+			+		
ZR5	+	+	+				+	
ZR6	+	+	+					+
ZR7	+	+	+	+				
ZR8	+	+	+		+			
ZR9	+	+	+			+		
ZR 11	+	+	+				+	
ZR 12	+	+	+					+

Compositions of the blends

The pigments were synthesized by the technology of solid phase sintering. A number of mixtures were prepared and a series of samples were synthesized at different combinations of raw materials. Rice husk ash was used as a source of SiO_2. Then 6% mineralizer (NH_4Cl) was added.

An important issue in the synthesis of pigments is the precise dosing of the different components and compliance with the recipe specified. The quantities of materials from the recipe for 100g blend were weighed with a precision of 0.1g, then they were dry mixed and homogenized in a PULVERISETTE–6 planetary mill, produced by FRITSCH.

The sintering was carried out in a laboratory muffle furnace at heating rate of 300-400°C/h in air, in closed porcelain crucibles with 3 h isothermal period at the final temperature. The pigments were sintered at 1000°C, 1100°C and 1200°C.

RESULTS AND DISCUSSION

Figure 1 presents photos of the starting composition as well as the synthesized pigments.

Fig. 1 Initial mixtures and synthesized pigments: in each composition the mixture is on the left, and the pigment synthesized at 1200°C is on the right

Color measurement

Color is one of the most important indicators of pigment quality. Colored substances absorb and convert light rays of a certain wavelength into the visible portion of the spectrum due to their atomic structure. The CIELab system defines the colors not only of ceramic pigments but also of other materials, which shows that this system is universal and widely used. In the present paper the color determination of the pigments is carried out spectrally with a tintometer of Lovibond Tintometer RT 100 Color. The colour measurements were performed using the CIELab method. This method, which is the standard for analyses in the ceramic industry, especially for ceramic pigments, allows the determination of the whiteness and colour degree of tiles by measuring three parameters: L*, a* and b*, where:

L* (brightness), from absolute white L* = 100 to absolute black L*= 0

a* - green color (-) / red color (+)

b* - blue color (-) / yellow color (+)

The color space of the CIELab system is shown in Figure 2.

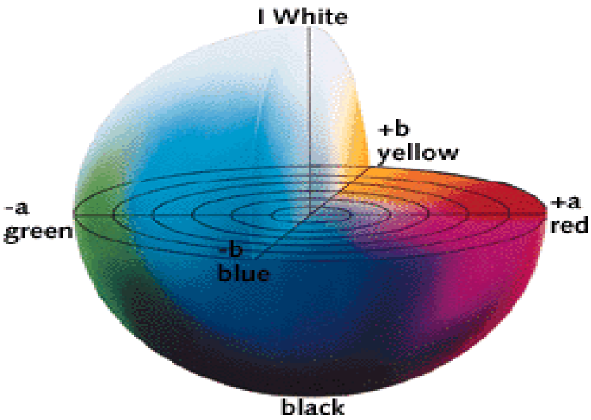


Fig. 2 Colour space of CIELab system

Tables 2 and 3 show the results from the conducted research.

Table 2. Results of color coordinate measurements in the CIELab system of zircon ceramic pigments with rice husks

№ of sample	T of sintering	Color	L	a *	b *
ZR 1	1000°C	tile red color	71.02	17.51	-3.06
	1100 °C		66.67	12.51	-6.72
	1200 °C		68.69	3.13	-14.76
ZR 7	1000°C	tile red color	48.38	13.77	1.67
	1100 °C		44.22	11.41	8.88
	1200 °C		47.26	7.07	5.32
ZR 2	1000°C	green	56.11	-4.08	22.38
	1100 °C		54.52	-3.23	21.26
	1200 °C		53.62	-1.09	19.68
ZR 8	1000°C	tobacco	50.00	7.67	22.2
	1100 °C		52,38	4.3	25.26
	1200 °C		54.38	2.77	25.70
ZR 3	1000°C		74.78	6.61	-12.65
	1100 °C	light purple	73.07	8.09	-10.04
	1200 °C	purple	62.76	9.16	-0.11

Table 3. Results of color coordinate measurements in the CIELab system of zircon ceramic pigments with rice husks

№ of sample	T of sintering	Color	L	a *	b *
	1200 °C	light purple	62.76	9.16	-0.11
ZR 9	1000°C	purple	75.68	6.17	-11.92
	1100 °C	dark purple	71.36	7.67	-12.27
	1200 °C		63.94	8.62	-1.38
ZR 5	1000°C	green	68.59	-6.00	7.13
	1100 °C		66.84	-5.89	8.06
	1200 °C		60.61	-5.76	8.87
ZR 11	1000°C	light green	67.58	-5.74	7.68
	1100 °C		65.69	-5.63	7.53
	1200 °C		60.94	-5.51	9.01
ZR 6	1000°C	dark gray	37.84	0.91	6.16
	1100 °C	gray	55.00	2.23	10.92
	1200 °C	gray	49.01	1.85	13.89
ZR 12	1000°C	dark gray	40.00	1.40	6.89
	1100 °C	gray	51.62	2.73	9.89
	1200 °C	gray	51.92	2.94	16.04

Infrared spectroscopy (FT-IR)

Fourier Transform Infrared spectroscopy (FT-IR) spectra provide information about the functional groups in a sample.

Infrared spectroscopy is based on the interaction of substances with electromagnetic oscillations with a certain frequency. The infrared region of the spectrum includes the interval with wavelengths λ from 1 to 1000 μm but only the interval with wavelengths from 1 to 25 μm is of practical importance.

Molecules contain atoms or groups of atoms that have their own oscillation with a specific frequency. Based on this frequency, the various atomic groups are detected and thus the structure of the molecule is determined [8].

The results of the FT-IR tests are given in Fig. 3 ÷ 6.

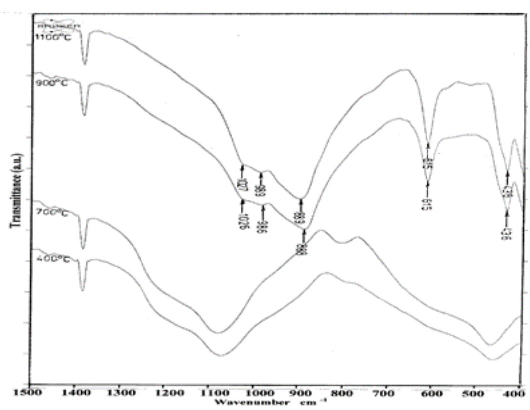
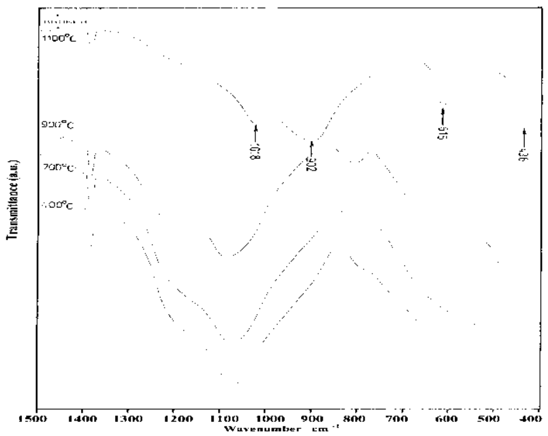


Fig. 3 FT-IR spectra with Co^{2+} chromophore

It was proved by X-ray analysis that at 900°C the main phase $ZrSiO_4$ is completely synthesized. In the case of pigments with a Co^{2+} chromophore, the band of zircon is observed even at 900° C. It is possible that the band at 986 cm^{-1} is due to isomorphic substitution of silicon or zircon atoms by a cobalt atom, as a result of which a Si - O - Co or Zr - O - Co bond is formed (Fig.



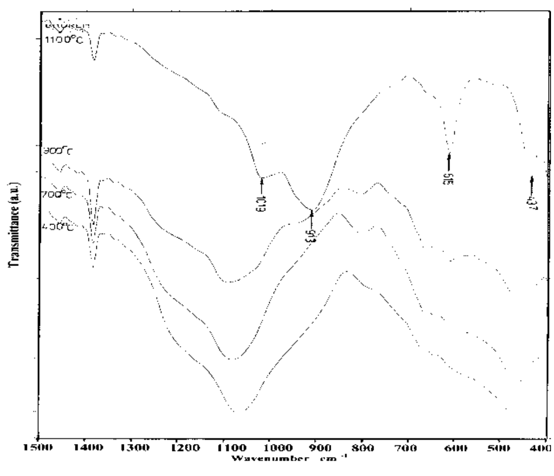
3).

Fig. 4 FT-IR spectra with Fe^{3+} chromophore

Fig. 5 FT-IR spectra with Mn^{2+}chromophore

In the systems with chromophores Fe^{3+} and Mn^{2+} the characteristic bands of zircon appear in the samples synthesized at 1100°C (Fig. 4, 5).

In the system with chromophores Cr^{3+} the spectra of the samples are almost identical, which proves the fact that up to 1100°C no zircon phase is synthesized (Fig. 6).



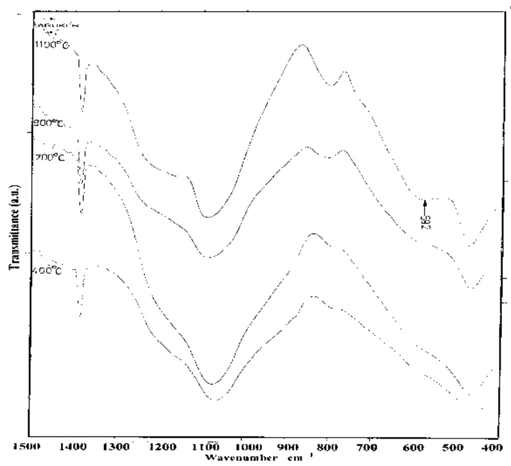


Fig. 6 FT-IR spectra with Cr^{3+} chromophore

The appearance of an absorption region of about 590 cm^{-1} may be related to the formation of the zirconium phase.

CONCLUSIONS

Zirconium ceramic pigments were synthesized by the method of solid state sintering.

The optimal parameters of synthesis of all compositions were determined.

As starting materials for the synthesis of zircon pigments, ZrO_2, Fe_2O_3, NH_4VO_3, Co_3O_4, Cr_2O_3, MnO_2, rice husk ash, and NH_4Cl as a mineralizer were used.

The most intense color appeared in composition ZR1, synthesized at 1000°C with an isothermal delay of 3 hours. This pigment had a tile-red color with a parameter:

(a *) = 17.51, measured by the CIELab system.

In all compositions, with the decrease in synthesis temperature, a decrease in their color intensity was observed.

It has been found out that the synthesized pigments can be successfully used in wall tile glazes.

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REFERENCES

1. Gerasimov E., A. Gerasimov, A. Atanasov, V. Toshev, D. Petkov, D. Ivanov, L. Georgieva, L.

Pavlova, N. Drenska, Vinarov P., Petrov P., Bachvarov S., Panova C., S. Bagarov, S. Serbezov, S. Stefanov., S. Dzhambazov, T. Stojkova, T. Datskova, H. Berlinov, Technology of Ceramic Products and Materials, Ed. S. Bachvarov, Saraswati IC, Sofia, 2003.
2. Eppler R. A., Zirconia-based colours for ceramic clazes, *Am.Cer. Soc. Bul.*, **2**, (1977), pp. 313–315.
3. Kleinrok D. et. al., Cpracowanie warunkow syntezy I stosowania barwnikow ceramocznych, *Szklo I Ceramika*, **7**, (1980), pp. 239–244.
4. Andreola F., L. Barbieri, F. Bondioli, Agricultural waste in the synthesis of coral ceramic pigment, *Dyes and Pigments*, **94**, (2), (2012), pp. 207–211.
5. Prasad C. S., K. N. Maiti, R. Venugopal, Effect of rice husk ash in whiteware compositions, *Ceram. Int.*, **27** (2001), pp. 629–635.
6. Andreola F., M. I. Martín, A.M. Ferrari, I. Lancellotti, F. Bondioli, J. Ma Rincón, M. Romero, L. Barbieri, Technological properties of glass-ceramic tiles obtained using rice husk ash as silica precursor, *Ceram. Int.*, **39** (2013), pp. 5427–5435.
7. Sobrosa F. Z., N. P. Stochero, E. Marangon, M. D. Tier, Development of refractory ceramics from residual silica derived from rice husk ash, *Ceram. Int.*, **43**, (9), 15, (2017), pp. 7142–7146.
8. Bellisola G., C. Sorio, Infrared spectroscopy and microscopy in cancer research and diagnosis, *Am. J. Cancer Res.*, **2**, (1), (2012), pp. 1–21.