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SYNTHESIS OF Co-Zn-Al-Ti-Cr SPINEL PIGMENT

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A synthesis of the green spinel pigment $\text{Co}_{3.7}\text{Zn}_{4.3}\text{Al}_{2.9}\text{TiCr}_{11.7}\text{O}_x$ by a new method of preparation has been investigated. All the samples of pigment were prepared by a two-step method of preparation. The influences of the raw material on the colour properties of the pigments were monitored. An STA Jupiter 449 apparatus (NETZSCH GmbH, Germany) was used for determination of the second step of the preparation. The colour of the pigments was measured in the visible region of light (400 – 700 nm) with a MiniScan (Hunter Lab, USA). The structures of prepared samples of pigment were studied by X-ray powder diffraction using D8 Advance equipment (Bruker, AXS, UK). The grain size distribution, specific weight, oil number and CPVC of the prepared samples were determined too.

Introduction

The Department of Inorganic Technology of the University of Pardubice is not only focused on synthesis of inorganic compounds that could find a practical use

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as pigments, but modification of methods of synthesis is investigated too. The problem of new methods of synthesis is very topical because of ecology, energy and economy reasons.

A high temperature process is almost always used for the preparation of inorganic pigments. This method is based on a reaction of solid phases. Oxides, hydroxides and other inorganic compounds are usually used as raw materials. The reaction is performed at high temperatures, up to 1300 °C, and an agent of mineralization is usually present.

The main aim of this research is the preparation of spinel pigment by a new method of synthesis, so-called MDR process, which consists of two steps of calcination. This process represents a simulation of "Mixer Dryer Reactor" at laboratory conditions. This method of preparation should decrease the calcination temperature necessary for obtaining a bright and clear hue of the pigments prepared.

Theory

Spinel pigments have been studied in our laboratory for many years. They belong to the group of mixed metal oxide pigments. Mixed metal oxide pigments can be considered as a subcategory of complex inorganic colour pigments. The name mixed metal oxides does not reflect the reality, as these pigments are not mixtures, but solid solutions or compounds consisting of two or more metal oxides. Each pigment has a defined crystal structure which is determined by the host lattice. Other oxides interdiffuse at high temperature into the host lattice structure by forming either a solid-state solution or a new compound [1]. Structurally, mixed metal oxide pigments belong to one of fourteen structure types [2,3]; the most common are the rutile and spinel ones.

Pigments with the spinel structure are widely used in ceramic and plastic industries. They cover a wide range of colours and many of them are thermally stable up to 1400 °C. They are resistant to molten glass. Another advantage is their mutual complete miscibility, allowing the user a choice of creating many intermediate hues [1].

Experimental

All the pigments were prepared by a nonstandard method of preparation. This method represents a simulation of "Mixer Dryer Reactor" at laboratory conditions. It is a two-step method. The first step represents form of intermediate product at a medium temperature. The intermediate was prepared by mixing of raw materials in suspension in a porcelain mortar and it was calcinated at 400 °C on a steel alloy

sheet. The second step represents classical calcination in an electric furnace at a suitable temperature for one hour.

The influence of the raw materials on the colour properties of the pigments was investigated. The pigments were prepared by the 8 different reactions.

Thermal analysis provided the first information about the temperature region of the formation of this pigment. Thermal analysis was carried out by means of STA Jupiter 449 equipment (NETZSCH, Germany) in temperature interval 20 – 1400 °C. We found out by thermal analysis that the pigment was formed around the temperature of 1100 °C based on result of thermal analysis.

The colour of the pigments was measured in the visible region of light (400 – 700 nm) with a MiniScan (Hunter Lab, USA). The measurement conditions were following: illuminant D65 (6500 K), 10° complementary observer and geometry of measurements d/8°, colour space CIE $L^*a^*b^*$ with difference ΔE^* [4]. The colour of the pigments is described by chroma (C) too. The pigments were measured in their applications into organic matrix in mass tone and in reduced tints in weight ratios 1:1 and 1:4 with TiO₂ (RG-15 — Precheza PLC, Přešov, CR) and into glaze G 07491 (Glazura Ltd., Roudnice nad Labem, CR). All prepared samples of the pigment Co_{3,7}Zn_{4,3}Al_{2,9}TiCr_{11,7}O_x were compared with the commercially produced pigment Green 410 (Shepherd Colour Comp., USA).

The structure of the pigments prepared was also investigated. The pigments prepared by calcination at temperatures 1050 and 1100 °C were studied by X-ray diffraction analyses, measured on a equipment diffractometer D8 (Bruker, GB), CuK α radiation, scintillation detector.

Physical-chemical analyses (particle size distribution, specific weight, oil number, CPVC) were carried out, too. In order to obtain pigments with the optimum particle sizes, the pigments were wet ground with ethanol and zircon corpuscles (1.8 mm in diameters) in a planetary mill Pulverisette 5 (Fritsch, GmbH Germany). The milling times were 10 minutes and 20 minutes. The particle size distribution was measured by means of a Mastersizer 2000 / MU (Malvern Instruments, UK). It is a highly integrated laser measuring system for analysis of particle size distribution. The equipment uses scattering of incident light on the particles. The signal is evaluated either on the basis of Mie scattering or Fraunhofer bending [5].

Specific weight is one of the basic physical-chemical parameters which characterize the powder substance. Its value was determined for the prepared pigments by pycnometric method [6]. Oil number was determined by standard method “mortar-pestle” [7]. The linseed oil was used like a binder. The values of CPVC (Critical Pigment Volume Concentration) were calculated from the specific weight and the oil number. CPVC characterizes a state when space among the particles of a pigment is just filled with the binder.

Results and Discussion

The colour of all the samples is green but there is a big difference between individual samples. Colour properties of the samples prepared at temperature 1050 °C and applied into organic matrix in mass tone are summarized in Table I. The difference ΔE_{CIE} between samples and standard applied into organic matrix in mass tone is large, but its values are expressively affected by values of brightness (L^*). Most of the prepared pigments are greener, but the large difference is between colour co-ordinates b^* which expressed the amount of blue and yellow hue. The value of co-ordinate b^* of the standard is in the field of blue hue. The pigment 8 has this co-ordinate in the field of blue hue too, but its colour especially in the mass tone is nearly turquoise. The value of chroma (C) of this pigment is markedly the highest. The pigments No. 5, 6 and 7 have the lowest values of the difference ΔE_{CIE} , but the value of their co-ordinate b^* is in the yellow field of hue.

The total colour difference (ΔE_{CIE}) between sample No. 2 and standard is higher, but the co-ordinates a^* and b^* are more positive. Based on the colour properties we can say that the pigment prepared by calcination of reaction mixture No. 2 is the most interesting.

Table I Color properties of the pigments $\text{Co}_{3,7}\text{Zn}_{4,3}\text{Al}_{2,9}\text{TiCr}_{11,7}\text{O}_x$ (mass tone)

No.	L^*	a^*	b^*	ΔE_{CIE}	C
Green 410	31.26	-17.05	0.46	0.00	17.06
1	33.15	-11.59	1.00	5.80	11.63
2	36.90	-17.64	0.28	5,67	17.64
3	37.00	-15.47	1.25	6.01	15.52
4	36.88	-19.45	0.24	6.11	19.45
5	35.99	-18.30	0.94	4.92	18.32
6	34.58	-15.39	1,48	3.85	15.46
7	35.99	-17.69	1.10	4.82	17.72
8	43.61	-22.86	-1.20	13.75	22.89

The results of colour properties of the pigments applied into organic matrix in reduced tints 1:1 and 1:4 are similar to the previous ones. All the pigments prepared are lighter than the standard Green 410, but, on the other hand, nearly all the pigments are greener and have a higher chroma than standard. Some of the samples show imperceptible colour deviation from the standard, but again there is a significant variety in the values of coordinate b^* .

Generally, we can say that the colour properties of pigment No. 2 are the closest to the colour properties of standard Green 410 and, on the other hand, the colour properties of pigments No 1 and 3 are not satisfactory enough. It can be

caused by using ZnCO_3 as raw material of zinc.

All the samples prepared by calcinations at $1050\text{ }^\circ\text{C}$ were applied into Glaze G 07491. The applications are glossy and without a cleavage. There is imperceptible difference in their colour. This pigment can be recommended for using in above mentioned unleaded glaze.

The samples (No. 2) of the pigment that were obtained by calcination at the

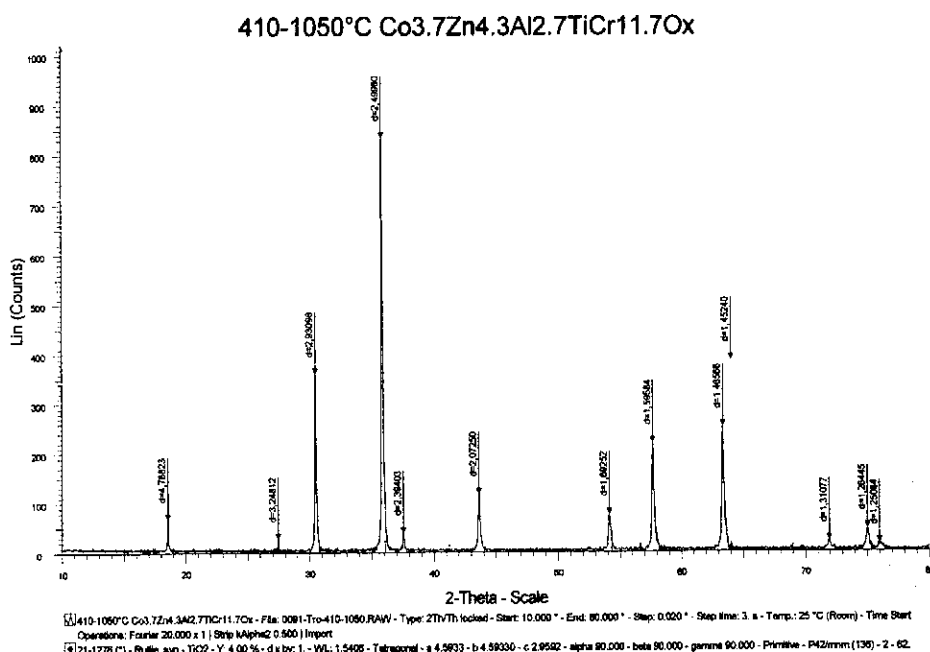


Fig. 1 The X-ray pattern of the sample No. 2 obtained by calcination at $1050\text{ }^\circ\text{C}$

temperatures 1050 and $1100\text{ }^\circ\text{C}$ were analyzed by powder X-ray diffraction. The results of analysis verified that crystalline structure of spinel is formed as early as at temperature $1050\text{ }^\circ\text{C}$. The diffraction pattern of sample No. 2 obtained by calcination at $1050\text{ }^\circ\text{C}$ is showed in Fig. 1. The system is biphasic and in addition to spinel phase there exists a phase of TiO_2 .

In Fig. 2 is diffraction pattern of sample No. 2 obtained by calcination at $1100\text{ }^\circ\text{C}$. The system is single-phasic and contains only the spinel phase.

Particle sizes and particle size distributions can markedly affect colour properties of inorganic pigments. That is why we tested sample No. 2 ($1050\text{ }^\circ\text{C}$) from this point of view. In this case the decrease in particle sizes markedly affects the colour properties of the pigment (Table II). The decreasing of particle sizes makes the pigment lighter, and this change is connected with higher value of

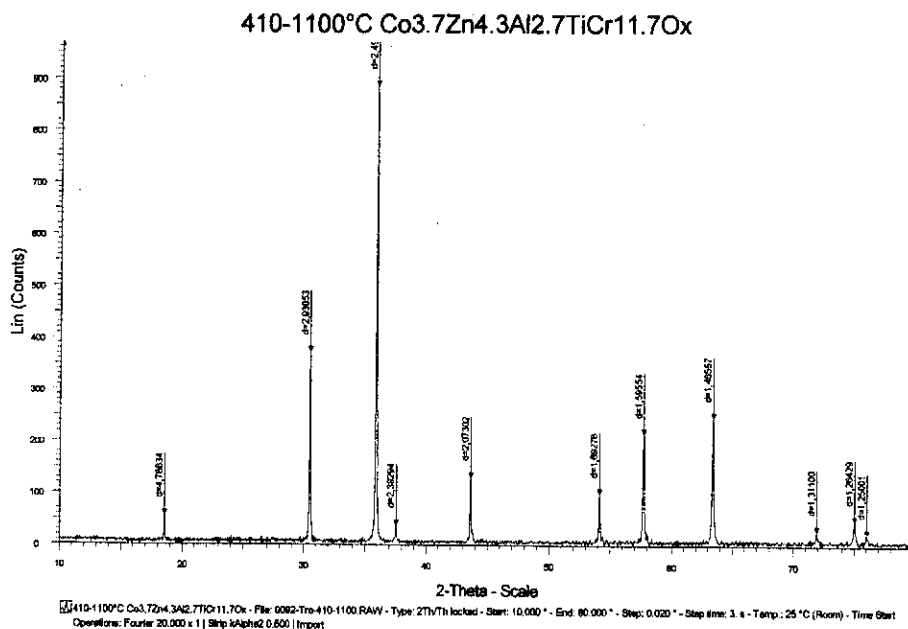


Fig. 2 The X-ray pattern of sample No. 2 obtained by calcination at 1100 °C

Table II The influence of grinding on the colour properties of sample No. 2 (application into organic matrix)

Grinding time	Application	L^*	a^*	b^*	C
0 minutes	Mass tone	36.9	-17.64	0.28	17.64
10 minutes	Mass tone	38.27	-19.46	-0.46	19.47
20 minutes	Mass tone	39.02	-19.74	-1.01	19.77
0 minutes	Reduced tint 1:1	63.41	-17.68	-1.74	17.77
10 minutes	Reduced tint 1:1	63	-19.63	-3.5	19.94
20 minutes	Reduced tint 1:1	61.6	-20.64	-3.13	20.88
0 minutes	Reduced tint 1:4	77.47	-12.82	-0.74	12.84
10 minutes	Reduced tint 1:4	75.07	-14.89	-4.1	15.44
20 minutes	Reduced tint 1:4	73.32	-16.45	-3.73	16.87

coordinate L^* in application into organic matrix in mass tone. At the same time the values of coordinate a^* decrease, and the pigment is greener. In applications in reduced tints, the values of coordinate b^* were shifted to the region of yellow colour in the colour space CIE $L^*a^*b^*$; it means that the values of coordinate b^* have positive sign. The pigments in reduced tints are darker and greener. After grinding, the pigments obtained higher chroma (C) than they had before.

Wet grinding in the planetary mill Pulverisette 5 in ethanol medium improved the grain size distribution of the pigment $\text{Co}_{3.7}\text{Zn}_{4.3}\text{Al}_{2.9}\text{TiCr}_{11.7}\text{O}_x$. The values of particle sizes of the standard and sample No. 2 before and after grinding are shown in Table III.

Specific weight of the pigments was measured pycnometrically. The values of specific weight of the prepared pigments $\text{Co}_{3.7}\text{Zn}_{4.3}\text{Al}_{2.9}\text{TiCr}_{11.7}\text{O}_x$ are in range from 3.90 to 4.12 g cm⁻³. Invariability of the pigment production is given by oil consumption. This parameter is in the range from 18.43 to 18.78 g/ 100 g of pigment for sample No. 2. The calculation of CPVC values is based on the knowledge of specific weight and oil consumption of a pigment. The values of CPVC of the samples are in a range from 55.18 % to 55.65 %.

Table III Particle sizes of sample No. 2

Grinding time	Particle sizes, μm		
	d_{10}	d_{50}	d_{90}
0 minutes	1.321	24.689	52.578
10 minutes	0.555	1.717	6.641
20 minutes	0.5	1.497	5.078

Conclusion

Nonstoichiometric spinel pigment $\text{Co}_{3.7}\text{Zn}_{4.3}\text{Al}_{2.9}\text{TiCr}_{11.7}\text{O}_x$ was prepared by a nonstandard method of preparation. The preparation was made in two steps. In the first step the suspensions of raw materials were calcinated at medium temperature of 400 °C in air. The temperature range of the second step was determined by thermal analysis of the obtained intermediates after the first step of MDR process.

The green spinel pigment $\text{Co}_{3.7}\text{Zn}_{4.3}\text{Al}_{2.9}\text{TiCr}_{11.7}\text{O}_x$ was prepared according to eight reaction equations. Each of the prepared pigments had green colour, but the difference between them was noticeable. The most acceptable composition of reaction mixture for preparation of this green pigment is following: CoCO_3 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, TiO_2 and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The total colour difference between standard Green 410 and this pigment (No. 2) is imperceptible. The presence of spinel crystalline structure in sample No. 2 was confirmed by powder X-ray diffraction. Although the analysis showed that the pigment prepared at temperature 1050 °C is biphasic, from the results of colour measuring we can recommend the temperature of the second step 1050 °C. Quite useful physical-chemical properties, suitable grain size distribution after 20 minutes of wet grinding and even thermal stability as well as chemical stability of prepared inorganic pigments with the spinel structure predestined these compounds for application into glazes, coatings or into plastics.

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References

- [1] Trojan M., Šolc Z, Novotný M.: *Pigments*, Kirk-Othmer Encyclopedia of Chem. Technol., p. 45, Vol. 19, J. Wiley and Sons Inc., New York, 1996.
- [2] DCMA - Classification and Chemical Description of the Mixed Metal Oxide Inorganic Coloured Pigments, Metal Oxides and Ceramic Color Subcommittee DCMA, 1982.
- [3] Buxbaum G.: *Industrial Inorganic Pigments*, p. 100, 112 – 114, VCH, Weinheim, 1993.
- [4] Šulcová P.: *Properties of Inorganic Pigments and Methods for their Evaluation* (in Czech), p. 14 – 37, University of Pardubice, Pardubice, 2000.
- [5] Šulcová P., Beneš L.: *Experimental Methods in Inorganic Technology* (in Czech), p. 109 – 114, University of Pardubice, Pardubice, 2002.
- [6] DIN ISO 787/10
- [7] DIN ISO 787/5