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

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Submitted September 17, 2004; accepted November 25, 2004

Keywords: Ceramic pigments, High-temperature pigments, Spinel

The main aim of the research was to propose, verify and analyze the conditions of synthesis of spinel pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$. The influences of the raw materials and the calcinate temperature on the colour properties of the prepared pigments were monitored. These pigments afford interesting green hue in ceramic glazes and in organic matrix. Mean particle sizes of the prepared pigments decreased after milling from values around 24 μm to 1.5 μm. The analysis of the X-ray diffraction patterns established that all the samples have a single phase cubic spinel structure. Some of the physical-chemical properties that characterize the prepared pigments (specific weight, oil number, CPVC) were also determined.

INTRODUCTION

Inorganic pigments have been studied at our workplace for many years [1, 2, 3]. The spinel pigments belong to the group of mixed metal oxides pigments. Mixed metal oxide pigments can be considered as a subcategory of complex inorganic colour pigments. The name, mixed metal oxides, does not represent 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 [4]. Structurally, mixed metal oxide pigments belong to one of fourteen structure types [5, 6]; the most common are 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 [7]. Another advantage is their mutually complete miscibility, allowing the user a choice of creating many intermediate colours [8, 9].

A high temperature process is almost always used for the preparation of inorganic pigments. This method is based on a reaction of solid phases [10]. Oxides, hydroxides and other inorganic compounds are usually used as raw materials. The reaction is performed at high temperature, up to 1300°C; an agent of mineralization is usually present. Next method, which is very often used for preparation of inorganic pigments, is based on milling activation. Some spinel compounds that are not used as pigments were also prepared by this ceramic technique [11]. The third method of preparation of pigments is the polymeric precursor method (Pechini) [12]. Nonstoichiometric green spinel pigment containing Co, Zn, Ti and Cr was prepared by a non-standard method of preparation which consists of two steps of calcinations. This method should incur to decrease of the calcination temperature necessary to reach bright and clear hues.

EXPERIMENTAL

All the pigments were prepared by a non-standard method of preparation. This method represents a simulation of "Mixer Dryer Reactor" in laboratory conditions. It is a two-step method. The first step represents the forming of the semi-products at middle temperature. The semi-products were obtained by mixing of raw materials in suspensions in a porcelain mortar and were calcined at 400°C at an alloy steel sheet. The second step represents classical calcinations in an electric furnace. The semi-products were calcined in corundum crucibles in an electric resistance furnace, with heating rate 10°C min^{-1}. The calcinations temperatures of 1100, 1200 and 1300°C were maintained for 1 h. The prepared pigments were applied into organic matrix in mass tone and in reduced tints in weight ratios 1:1 and 1:4 with TiO_2 (RG-15, Precheza a.s., Přerov, CR) and into glaze P 07491 (Glazura s. r. o., Roudnice nad Labem, CR).

The influence of raw materials on the colour properties of the pigments was investigated. The pigments

Paper presented at the conference Solid State Chemistry 2004, Prague, September 13 -17, 2004.

were prepared from four starting mixtures. The first mixture contained $CoSO_4.7H_2O$ and $CoCO_3$ (in ratio 2.9:0.7), $ZnSO_4.7H_2O$, $Na_2Cr_2O_7.2H_2O$ and TiO_2. The second mixture contained the same materials, only the ratio between $CoSO_4.7H_2O$ and $CoCO_3$ was 3.25:0.35. The third mixture contained $CoSO_4.7H_2O$, $ZnSO_4.7H_2O$, $Na_2Cr_2O_7.2H_2O$ and TiO_2. And the fourth mixture contained $CoSO_4.7H_2O$ and $CoCO_3$ (in ratio 3.25:0.35), $ZnSO_4.7H_2O$, $Na_2Cr_2O_7.2H_2O$ and $Na_2Ti_4O_9$.

The thermal analysis provided the basic information about the temperature region of the formation of this pigment. Thermal analysis was carried out by equipment STA Jupiter 449 (NETZSCH, Germany) in temperature region 20-1400°C.

The colour of the pigments applied into organic matrix was measured in the visible region of light (400-700 nm) with 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** [13]. The colour of the pigments is also expressed by chroma.

The structure of the prepared pigments was also investigated. The prepared pigments were studied by X-ray diffraction analyses. X-ray analyses were measured by equipment diffractometer D8 (Bruker, GB), CuK_α radiation, scintillation detector.

Physical - chemical analysis (particle size distribution specific weight, oil number, CPVC) were also determined. In order to obtain the pigments with optimal particle sizes, the pigments were wet ground with ethanol and zircon corpuscles (1.8 mm in diameters) in planetary mill Pulverisette 5 (Fritsch, GmbH Germany). The milling times were 10 and 20 minutes. The particle size distribution was measured by Mastersizer 2000/MU (Malvern Instruments, UK). It is a highly integrated laser measuring system for analysis of particle size distribution. The equipment uses the scattering of incident light on particles. The signal is evaluated either on the basis of Mie scattering or Frauenhofer bending [14].

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 [15]. Oil number was determined by standard method "mortar-pestle" [16]. The linseed oil was used like a binder. The values of CPVC (Critical Pigment Volume Concentration) [16] 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

We determined that the pigment takes form around temperature 1200°C based on result of thermal analysis. That is why the temperature range of the second step of preparation between 1100 and 1300°C was chosen. All the prepared samples of the pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ were compared with commercially produced pigment Green 179 (Shepherd Color Comp., USA). The colour of the samples is green but there is a big difference between individual samples. Colour properties of the samples applied into organic matrix in mass tone are summarized in table 1. Calcination temperature 1300°C of reaction mixture No. 4 caused deteriorating of the sample. As the sample was sintered, it can not be applied into organic matrix and therefore it is not put in the table 1. The values of coordinate *L** (brightness) decreases with the growing temperature. It means that the samples prepared at temperature 1100°C

Table 1. The colour properties of the prepared samples of the pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ (an application into organic matrix in mass tone).

Pigment sample	Temperature (°C)	*L**	*a**	*b**	ΔE^*_{CIE}	*C*
Green 179	-	35.47	-16.27	2.05	0.00	16.40
1	1100	38.00	-18.32	3.92	4.59	18.73
2	1100	38.57	-19.52	3.23	4.93	19.79
3	1100	38.75	-18.64	3.77	5.23	19.02
4	1100	37.70	-18.73	4.13	5.58	19.18
1	1200	35.96	-16.57	3.61	0.68	16.96
2	1200	35.84	-16.40	3.48	0.41	16.77
3	1200	36.66	-17.50	3.85	2.51	17.92
4	1200	35.73	-15.23	4.40	2.46	15.85
1	1300	32.67	-12.96	3.83	6.52	13.51
2	1300	32.69	-13.11	3.91	6.50	13.68
3	1300	31.92	-11.95	3.27	6.35	12.39

are lighter then the samples prepared at higher temperature. At the same time pigments prepared at lower temperature acquire higher amount of green hue. Values of coordinate *C* (chroma) of the samples prepared by calcination at temperature 1200°C are similar to values of coordinate *C* of the standard Green 179. Based on the investigation and evaluation of colour properties of the samples, we can say, that the temperature 1200°C is the best temperature for preparation of this green pigment.

Based on the values of ΔE^*_{CIE}, we can say that the pigment prepared from mixture No. 2 is colourfully comparable with the standard Green 179 and the difference between them is imperceptible ($\Delta E^*_{CIE} = 0.41$).

The difference between colours of the samples and the standard in reduced tints is more expressive. The pigment 2 applied into organic matrixes in reduced tints has greener hue than standard and its chromes are the highest. Although the values of ΔE^*_{CIE} of the sample 3 (in tint 1:1, $\Delta E^*_{CIE} = 2.93$) and sample 1 (in tint 1:4, $\Delta E^*_{CIE} = 1.66$) are the lowest, the sample 2 (in reduced tint 1:1, $\Delta E^*_{CIE} = 3.83$), (in reduced tint 1:4, $\Delta E^*_{CIE} =$ = 1.98) was chosen as the best sample of pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ because of its higher value of chroma that caused the deeper colour and because its coordinates a* and b* have more appropriate values.

All the samples that were prepared by calcination at 1200°C were applied into Glaze P 07491. Applications are glossy and without cleavages. Colours of all applications are very similar and there is no visible difference between each other. The lowest total colour difference is again between the pigments No. 2 and standard Green 179 ($\Delta E^*_{CIE} = 2.57$). This pigment can be recommended for using in above mentioned unleaded glaze.

The samples (No. 2) of the pigment that were obtained by calcinations at temperature 1100 and 1200°C were analyzed by powder X-ray diffraction. The analysis of the X-ray diffraction patterns established that the samples have a single phase. The diffraction pattern of sample No. 2 obtaining by calcination at 1100°C is showed in figure 1. The lattice parameter of cubic spinel structure (a) is 0.8328 nm. The same result was obtained by analysis of the pigment prepared at temperature 1200°C.

The particle sizes and particle size distributions can markedly affect the colour properties of inorganic pigments. That is why the prepared samples were tested from this point of view. The main aim was to decrease the particle sizes and monitor the influence of particle sizes on the colour properties of the pigment.

In this case the decreasing of particle sizes did not markedly affect the colour properties of the pigment, but there is a little difference in values of colour coordinates notably in applications into organic matrix in reduced tints (table 2). The decreasing particle size makes pigment lighter and this change is connected with higher value of 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. After grinding the pigments acquired higher chroma then previously.

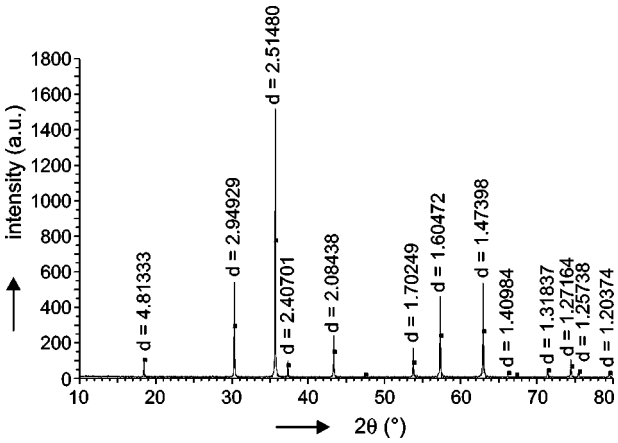

Figure 1. The X-ray pattern of the sample No. 2. obtaining by calcination at 1100°C.

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

Grinding time (min)	Application	*L**	*a**	*b**	*C*
0	Mass tone	35.84	-16.40	3.48	16.77
10	Mass tone	37.24	-17.95	4.03	18.40
20	Mass tone	37.92	-18.11	4.14	18.58
0	Reduced tint 1:1	62.12	-18.33	-0.13	18.33
10	Reduced tint 1:1	62.73	-18.48	0.21	18.48
20	Reduced tint 1:1	61.08	-19.05	1.13	19.08
0	Reduced tint 1:4	76.10	-13.49	-1.48	13.57
10	Reduced tint 1:4	75.25	-13.63	0.24	13.63
20	Reduced tint 1:4	72.50	-14.81	0.55	14.82

Wet grinding in the planetary mill Pulverisette 5 in ethanol medium leads to decreasing of the particle size of the pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$. The values of particle sizes of the sample are shown in table 3.

The specific weight of the pigments was measured pycnometrically. The specific weight of the prepared pigments $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ 4.43 to 4.63 g/cm^3 is slightly higher than that of the reference compound Green 179 (4.74 g/cm^3). Invariability of the pigment production is given by oil consumption. This parameter is for prepared pigments in the range from 11.25 to 12.76 g/100 g and it is comparable with reference compound Green 179 (11.94 g/100 g). 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 prepared pigments are in a range from 60.59 % to 63.56 %. It is corresponding with *CPVC* of the reference compound Green 179 (*CPVC* = 62.18 %).

Table 3. Particle sizes of the sample No. 2.

Grinding time (min)	Particle sizes (μm)	
	Particle size range	Mean particle size
0	1.3 - 53	24.7
10	0.6 - 6.6	1.7
20	0.5 - 5.1	1.5

CONCLUSIONS

Nonstoichiometric spinel pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ was prepared by a non-standard method of preparation. The preparation was made in two steps. In the first step the suspensions of raw materials were calcined at middle temperature of 400°C on 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 affect of initial raw materials was observed. The physical-chemical properties of the prepared pigments were determined. These properties are important for application of the pigments. The prepared samples of pigment were compared with commercially produced green spinel pigment named Green 179 (Shepherd Color Comp., USA). The pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ was prepared according to four 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: $CoSO_4.7H_2O$, $CoCO_3$, $ZnSO_4.7H_2O$, $Na_2Cr_2O_7$. $.2H_2O$ TiO_2 and $Na_2Cr_2O_7$. The total colour difference between standard Green 179 and this pigment (No. 2) is imperceptible. The presence of spinel crystalline structure in the sample No. 2 was verified by powder X-ray diffraction. Although the analysis validated that spinel structure is formed by firing of sample at temperature 1100°C, based on the results of colour measuring we recommend the temperature of the second step of calcination 1200°C.

Quite usable physical-chemical properties comparable with reference compound commercially produced pigment Green 179, suitable grain size distribution and even thermal stability of prepared inorganic pigments with the spinel structure predestined these compounds for application into glazes, coatings or into plastics.
This two-step method is a good way of preparation of high quality inorganic pigments. The method can decrease the calcinate temperature necessary for reaching bright and clear hues.

Acknowledgement

The work was supported by Grant Agency of Czech Republic, by grant No. 104/02/1443. Authors thank to doc. Ludvík Beneš, CSc. for X-ray crystallography and to Shepherd Color Company for providing of the pigment Green 179.

References

1. Trojan M., Beneš L.: Materials Letters *8*, 247 (1984).
2. Šolc Z., Trojan M., Kuchler M.: Termochimica Acta *92*, 463 (1985).
3. Šulcová P., Trojan M.: Dyes and Pigments *58*, 59 (2003).
4. Trojan M., Šolc Z, Novotný M.: *Pigments, Kirk-Othmer Encyclopedia of Chemiacl Technology*, p. 45, Vol. 17, J. Wiley and Sons Inc., New York 1995.
5. DCMA - Clasification and Chemical Description of the Mixed Metal Oxide Inorganic Colored Pigments, Metal Oxides and Ceramic Color Subcommitte DCMA, 1982.
6. Buxbaum G.: *Industrial Inorganic Pigments*, p. 100, 112-114, VCH, Weinheim 1993.
7. Emel O., Servet T.: Journal of the European Ceramic Society *23*, 2097 (2003).
8. Gui-Qin Y., Bing H., Zheng-Tao S., Le-Mei Y. and Xiu-Yu W.: Dyes and Pigments *55*, 9 (2002).
9. Llusar M., Forés A., Badenes J. A., Calbo J., Tena M. A., Monrós G.: Journal of the European Ceramic Society *21*, 1121(2001).
10. Šulcová P., Trojan M.: Dyes and Pigments *44*, 165 (2000).
11. Ahmed M. A., Ateia E., El-Dek S. I.: Vibrational Spectroscopy *30*, 69 (2002).

12. Candeia R. A., Bernardi M. I. B., Longo E., Santos I. M. G., Souza A. G.: Materials Letters *58*, 569 (2004).
13. Šulcová P.: *Properties of inorganic pigments and methods of their evaluation* (in Czech), 1st ed., p. 14-37, Pardubice 2000.
14. Šulcová P., Beneš L.: *Experimental methods in inorganic technology*, 1st ed., p.109-114, Pardubice 2002 (in Czech).
15. DIN ISO 787/10
16. DIN ISO 787/5

PODMÍNKY SYNTÉZY SPINELOVÉHO PIGMENTU Co-Zn-Ti-Cr

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Hlavním cílem výzkumu bylo nalézt, ověřit a rozpracovat podmínky syntézy spinelového pigmentu $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$. Byl sledován vliv výchozích surovin a teploty kalcinace na barevné vlastnosti připravených pigmentů. V keramické glazuře a organickém pojivovém systému poskytuje tento pigment zajímavý zelený odstín. Střední hodnota velikosti částic připravených pigmentů byla mletím snížena z hodnoty kolem 24 μm na 1.5 μm. Rentgenovou difrakční analýzou bylo prokázáno, že všechny připravené vzorky mají jednofázovou kubickou spinelovou strukturu. Byly stanoveny také některé fyzikálně-chemické vlastnosti připravených pigmentů (měrná hmotnost, olejové číslo, KOKP).