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Ceramic Pigments on the Base of the CoO–ZnO–SiO_2 System Obtained by a Sol–Gel Method

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Abstract: Preparation of a cobalt pigment based on the systems CoO–ZnO–SiO_2 by a sol–gel method has been studied. Sol–gel preparations were compared with conventional ceramic solid state synthesis. The samples were heat-treated within the temperature range of 200°–1200°C and analysed by X-ray diffraction and infrared spectroscopy. It was established that the application of the sol–gel method lowered the synthesis temperature of the pigments. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Cobalt silicate-based ceramic pigments are widely used for coloured glazes in the ceramic industry.[1–3] They are characterized by having a high resistance with respect to light, environment, high temperature and chemicals. In contrast to CoO, cobalt silicates are well dispersed in glazes and coatings.[4] Some improvement to the conventional way of preparation of blue pigments is achieved by solid state interaction of SiO_2, CoO and ZnO in the temperature range 1100–1300°C.[1] Mineralizers—NaF, H_3BO_3—are used successfully in amounts of 3–5%.[4–7] During the past years investigations have been performed on the synthesis of pigments by non-conventional methods such as sol–gel technology.[8–10] The purpose of the present paper is a continuation of our previous study[9] for preparation of cobalt pigments at lower temperature, but extending sol–gel methods to more complicated systems such as CoO–ZnO–SiO_2. The next step will be to add these pigments to some very chemically active low melting frits which have been prepared recently[11] for special decorative applications.

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2 EXPERIMENTAL

Two schemes were used for obtaining pigment with the composition 2CoO–2ZnO–SiO_2: (i) conventional thermal treatment of ceramic batches; (ii) gels calcined at high temperature. The succession of the processes is shown in Fig. 1(a) and (b). The initial substances used were $Co(NO_3)_2$, $Zn(NO_3)_2$, sol of SiO_2, Co_3O_4, ZnO and SiO_2. By acidification of water glass a stable SiO_2-sol is obtained. pH values in the aqueous solution are limited to 3 by adding HCl acid. For purification dialysis was performed for 7 h until all ions are removed. It was established analytically that 100 ml of sol contained 9.7 SiO_2.

Mixing the SiO_2 sol with salt solutions containing Co^{2+} and Zn^{2+} ions reduces electrostatic repulsion between the particles. As a result, the aggregates gel. This is one of the classical methods of sol–gel technology following the scheme of Fig. 1(b).[13–16] The phase transitions in the gels and in the batches during the chemical reaction were investigated by X-ray analysis (a DRON-2TM apparatus, CuK_α radiation). The phases were identified using the standard X-ray data published in JCPDS. IR spectra were recorded on a two beam spectrophotometer (SPECORD M 80) in the range

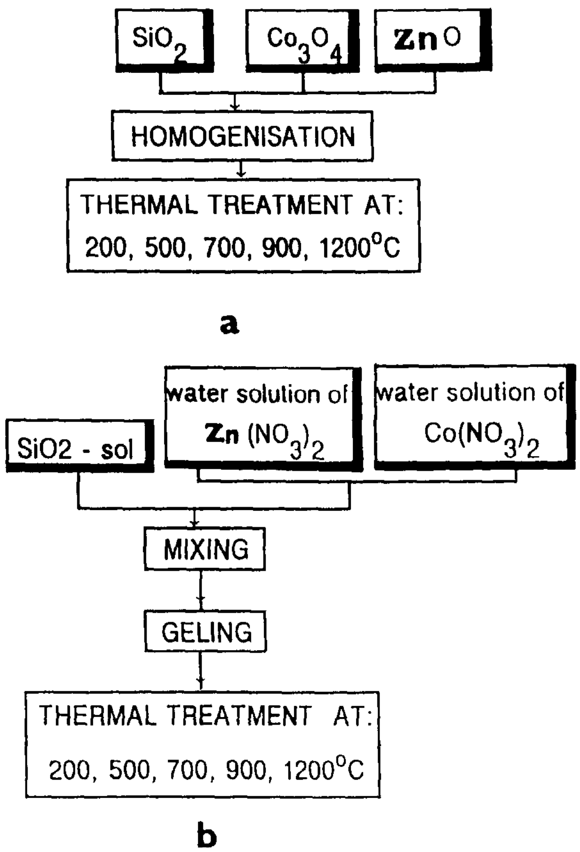

Fig. 1. Two variants for obtaining pigments: (a) conventional ceramic technology; (b) sol–gel method.

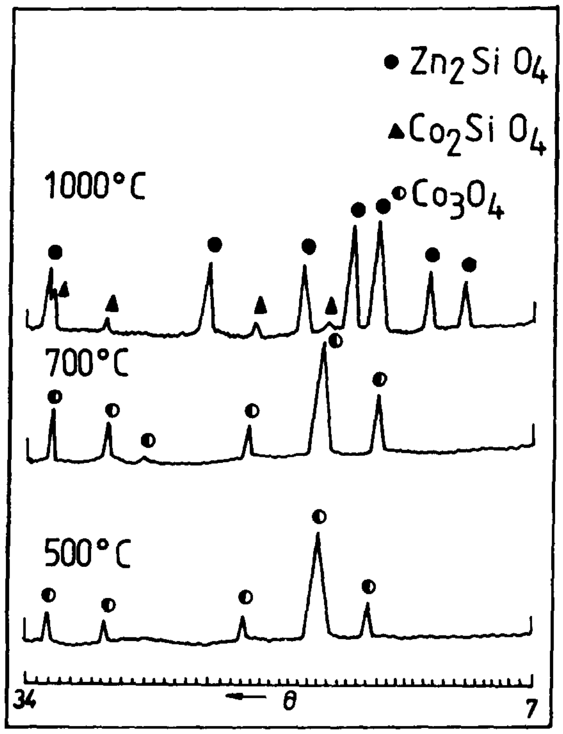

Fig. 2. Diffractograms of the samples obtained by the conventional ceramic technology.

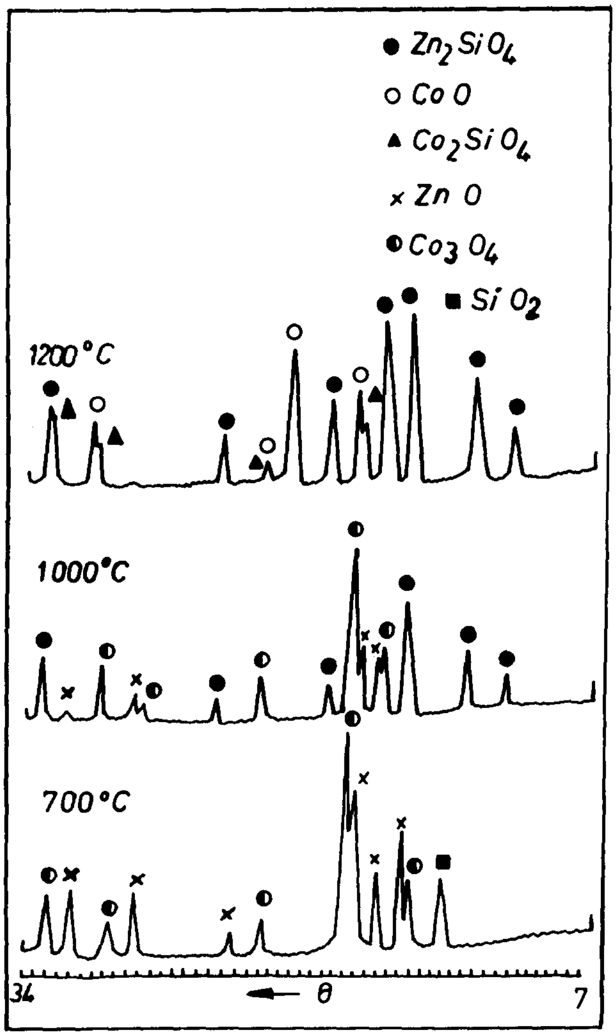

Fig. 3. Diffractograms of the samples obtained by sol–gel method.

1300–300 cm^{-1}. The samples have been spectrally investigated in liquid paraffin suspensions. The colorimetric measurements were performed with a an 'SPECOL 11', model colorimeter using the D 65 light source and detector at 2°. The CIELAB (L^*,a^*,b^*) chromatic co-ordinates were calculated from the reflectance curves obtained.

3 RESULTS AND DISCUSSION

The diffraction patterns of the samples prepared by the conventional ceramic method (see Fig. 1(a)) are presented in Fig. 2. Up to 700°C only diffraction peaks of the initial component, Co_3O_4. At 1000°C, the beginning of the synthesis is established for a silicate with a willemite structure together with CoO and Co_2SiO_4.

The diffraction patterns of the pigment obtained by the sol–gel method (see Fig. 1(b)) are presented in Fig. 3; phase formation occurs in a different way. At room temperature the material is amorphous. At 500 and 700°C the main crystalline phase is Co_3O_4. At 1000°C the major crystalline phase is Zn_2SiO_4 (willemite) and small amount of Co_2SiO_4. As the CoO in the initial batch is calculated to be 33.3 mol% it is evident that part is dissolved in the willemite structure, because the

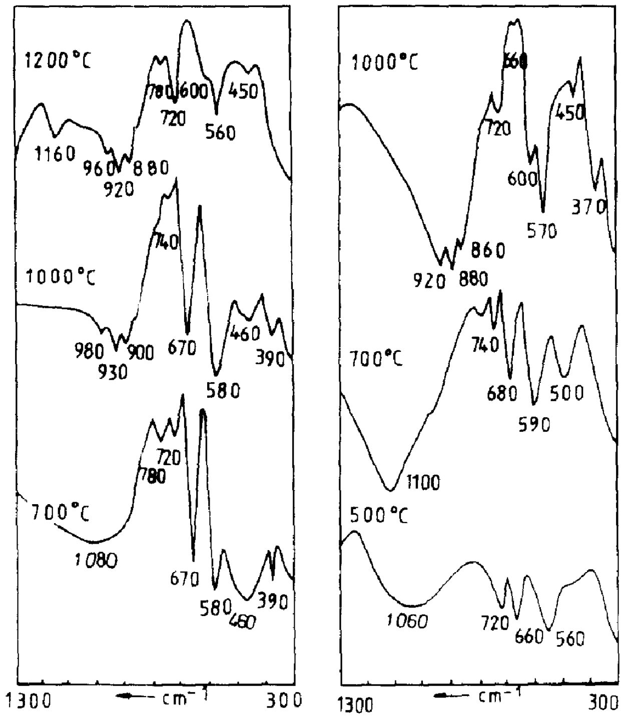

Fig. 4. IR spectra of the heat treated samples: (a) gels; (b) batches of oxides.

Table 1. Colorimetric characteristic of the pigments including in the frits for tiles

Composition of the glazes including frits according[11]	λd,nm	P_c,%	C^*_{ab}	L^*_{ab}	P_e,%
Frit D+5% pigment $2CoO.2ZnO.SiO_2$	468	6	19.1	39.6	26
Frit A+5% pigment $2CoO.2ZnO.SiO_2$	472	7	11.0	26.1	22

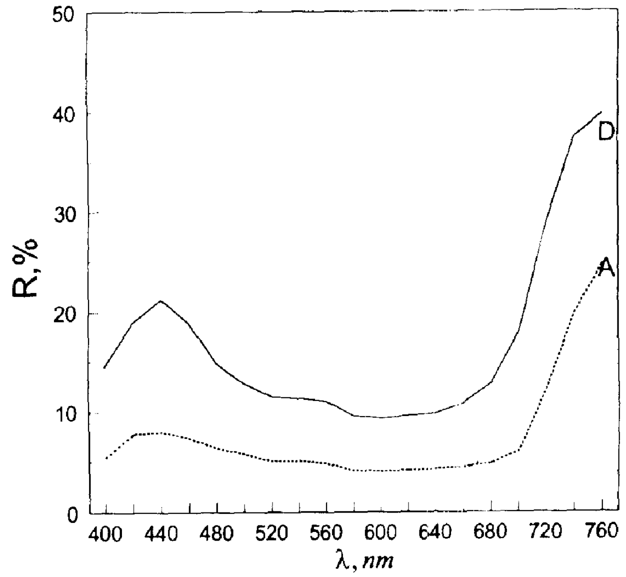

Fig. 5. Spectral reflectance curves of glazes of frits D and A firing at 600°C.

content of Co_2SiO_4 at high temperature as a independent phase is less than 10% (taking into account the low intensity of the strongest reflection at 2.47 Å). According to other investigations limited solid solutions form between Zn_2SiO_4 and Co_2SiO_4.[14] This is the reason for the production of blue pigment in the system CoO- ZnO-SiO_2 by traditional ceramic methods. In our case using gel technology, we decreased the temperature of the synthesis in comparison to classical technology. The obtained results are better also than that for the gels obtained previously in the pure CoO-SiO_2 system.[9]

The infrared spectroscopy studies have given additional information on the bonding between the structure units in the gels and the crystallized product. Up to 700°C the IR spectra of the gel material (Fig. 4(b)) exhibit absorption maxima around 660 cm^{-1} characteristic for Co_3O_4. Its disappearance in the spectra of heat-treated samples between 700–1000°C shows that a chemical interaction occurs.

The absorption maxima at 1100 cm^{-1} may be assigned to stretching modes of Si–O bands of polymerized SiO_2 tetrahedra. Initially SiO_2 remains as an amorphous phase. The spectra change considerably at 1000°C and are in good agreement with X-ray data discussed above. The position of the bands at 920–860 and 600–450 cm^{-1} may be ascribed to vibrations of the silicate tetrahedra in the willemite structure. This is in accordance with the spectra published many years ago for orthosilicates.[18–21] The IR spectra of the material obtained by the solid state reaction up to 700°C (Fig. 4(a)) show the presence of absorption maxima for Co_3O_4. Only at 1200°C Co bands at 920–860 cm^{-1} and 600–450 cm^{-1} predominate which are due to the vibrations of silicate tetrahedra.

The colorimetric properties are presented in Table 1 and Fig. 5. It is evidenced that obtained blue pigment may be used for glazing of floor and wall tiles. Similar results have been published recently for a variety of pigments obtained with others precursors.[21]

4 CONCLUSION

As a result of the experimental studies it may be noted that a polycrystalline material with the qualities of a blue pigment has been obtained at low temperatures in the CoO–ZnO–SiO_2 system by the sol–gel technology and the applicability of this method for the synthesis of pigments is demonstrated.

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REFERENCES

1. KALINSKAYA, T. V., LOBANOVA, L. B., SKORODUMOVA, N. A. & PODYACHEVA, T. I., *Laki*, **2**(4) (1988) 31.
2. HUMMEL, F. A. & SARVER, J. F., Jr, Swiss Patent 522723.
3. HUMMEL, F. A. & SARVER, J. F., Jr, USA Patent 3725102.
4. ALARCON, I., *Trans. Brit. Ceram. Soc.*, **84**(5), (1985) 170.
5. KVYATKOVSKAYA, K. K., ZACHIGIN, A. G. & KOSORUKOVA, E. C., *Steklo i Keramika* (In Russian), **4**(21) (1987).
6. PISCH, I. V., ROTMAN, T. I., ROMANENKO, Z. A. & CHIANOVSKAYA, E. N., *Steklo i Keramika* (In Russian), **4**(23) (1987).
7. BELENKII, E. I. & RISKIN, I. V., *Chimia and Technologya Pigmentov*. Chimiya, Leningrad, 1974, p. 656.
8. FERRER, L., SALES M. & ALARCON, I., In *Third Euro-Ceramics*, ed. P. Duran & J. Fernandez. Faenza Editrice Iberica S. L., 1993, p. 285.
9. DJAMBAZOV, S., NIKOLOV, R., DEREDJAN, A., IVANOVA, Y., DIMITRIEV, Y. & KASHCHIEVA, E., In *Qualicer, 94*. Castellon, 1994, p. 117.
10. IVANOVA, Y., GEORGIEVA, L., KASHCHIEVA, E. & SAMUNEVA, B., In *Third Euro-Ceramics*, ed. P. Duran and J. Fernandez. Faenza Editrice Iberica S. L., 2, 1993, p. 923.
11. DJAMBAZOV, S., NEDELCHEV, N., DIMITRIEV, Y., IVANOVA, Y. & YOLEVA, A., In *Proc. 2 Intern. Ceramics Congress*, ed. M. Ovecogen & H. Yaparlar. Istanbul, 1994, p. 216.
12. ILER, R. K., *The Chemistry of Silica*. John Wiley, New York, 1979.
13. ZARZYCKI, J., In *Disordereal Systems and New Materials*, ed. M. Borisov, N. Kirov & A. Vavrek. World Scientific, Singapore, 1988, p. 151.
14. NAVROTSKY, A., *J. Solid State Cem.* **6**(21) (1973).
15. DURAN, A., *Bol. Soc. Esp. Ceram. Vidr.*, **25** (1986) 395.
16. COLOMBAN, P. H., In *Advances in Ceramics Vol. 21, Ceramic Powder Science*. The American Ceramic Society, 1987, p. 139.
17. DOBRAVSKA, S. & SKRAND, Z., *Sular a Keramik*, **34** (1984) 133.
18. LAZAREV, A. N., *Kolebatelnie Spectri i Stroenie Silikatov*. Nauka, Leningrad, 1968, p. 223.
19. TART, P., *Spectrochim. Acta*, **19** (1963) 25.
20. PLOUSNINA, I. I., *Infrakrasnie Spectri Mineralov*. Moskva, 1977, p. 142.
21. MONROS, G., TENA, M. A., ESCRIBANO, P., CANTAVELLA, V. & CARDA, J., *Journ. Sol-gel Sci and Techn.*, **2** (1994) 377.