# CERAMIC PIGMENTS ON THE BASE OF COBALTOUS SILICATE OBTAINED BY SOL-GEL METHOD

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## ABSTRACT

Comparative investigations for obtaining of ceramic pigment on the base of cobaltous silicate were carried out using a classical melting technology and two variants of the sol-gel method. The precursors for the synthesis were $SiO_2$, CoO, silica hidrosol, TEOS and $Co(NO_3)_2$. The phase changes in the samples were studied in the temperature range from 200 to 1200°C using X-ray diffraction analysis, IR-spectroscopy and electron microscopy.

It was established that the sol-gel method decreases the temperature of synthesis.

## INTRODUCTION

Latterly, the ceramic pigments on the base of cobaltous silicate are widely used as colouring agents for glazes in the ceramic industry [1,2,3]. Their characteristics, such as high thermo- and chemical resistance, high tinting strength and light-permeability, as well as their good dispersion into glazes make these pigments preferable to CoO itself. For this reason, the control of the process of $Co_2SiO_4$ synthesis is of essential importance for the improvement of the quality of the pigments and ceramic products.

The synthesis of the pigments on the base of cobaltous silicate might be realized by a classical ceramic method [4,5], as well as by the sol-gel method [6].

Compared to the conventional ceramic method, the sol-gel one permits a lower synthesis temperature to be achieved and a monophase product to be obtained.

The aim of this study is to carry out a comparative research of the phase forming during the process of thermal treatment by the different synthesis methods.

## EXPERIMENTAL

The three methods of synthesis are used which are presented in FIG. 1

a) conventional ceramic method

b) sol-gel method version-I, where the $SiO_2$ is added in the form of TEOS and the CoO as a water solution of $Co(NO_3)_2$

c) sol-gel method version-II, where the $SiO_2$ is added in the form of $SiO_2$ sol.

The phase changes in the gels were studied by X-ray diffraction analysis (apparatus DRON-2TM); $Cu/K_\alpha$ radiation; IR-spectroscopy (SPECORD apparatus; carried out on powder samples in the 1200 to 400 $cm^{-1}$ range); DTA (Paulik-Paulik apparatus; heating rate 10°C/min; reference substance $Al_2O_3$) and Electronic microscopy (SEM-505 apparatus).

Standard X-ray diffractograms published in ASTM (N° 15-497 and N° 15-865 for $Co_2SiO_4$-I and for $Co_2SiO_4$-II respectively) were used.

## RESULTS AND DISCUSSIONS

The X-ray diffractograms of the samples obtained by the conventional ceramic method (see FIG.1- "a") are shown in FIG.2.

Up to the temperature of 900°C the characteristic diffractometric data of the initial components $Co_3O_4$ and $SiO_2$-=quartz are registered. At the temperature of 1000°C starts the process of partial reduction:

$$Co_3O_4 \rightarrow CoO + O_2.$$

In the whole temperature interval of the treatment, the forming of significant quantities of $Co_2SiO_4$ is not found.

The X-ray diffractograms of the sample obtained by the sol-gel method version-I (TEOS) (see FIG.1 - "b") are shown in FIG.3. At the temperature of 200°C the samples are amorphous. The initial process of the formation of Co-silicate is registered at 900°C. At a higher temperature (1000°C) the transformation of $Co_2SiO_4$-I into $CoSiO_4$-II is going off; free $SiO_2$ crystobalite is still available. Near to 1200°C the product is almost monophase $CoSiO_4$-II. This result is similar to the results reported by Larsen et al.[7].

The X-ray diffractograms of the samples obtained by the sol-gel method version-II (see FIG.1 - "c") are shown in FIG.4. In this case the process of phase forming is different. Up to 900°C the main crystal phase in the samples is $Co_3O_4$. At 1000°C, $SiO_2 \propto$-quartz, $Co_3O_4$ and $Co_2SiO_4$ are presenting separately. The sample remains polyphase in the studied temperature interval.

The mechanism of phaseforming as a function of the temperature changes by the different studied versions is shown in FIG.5.

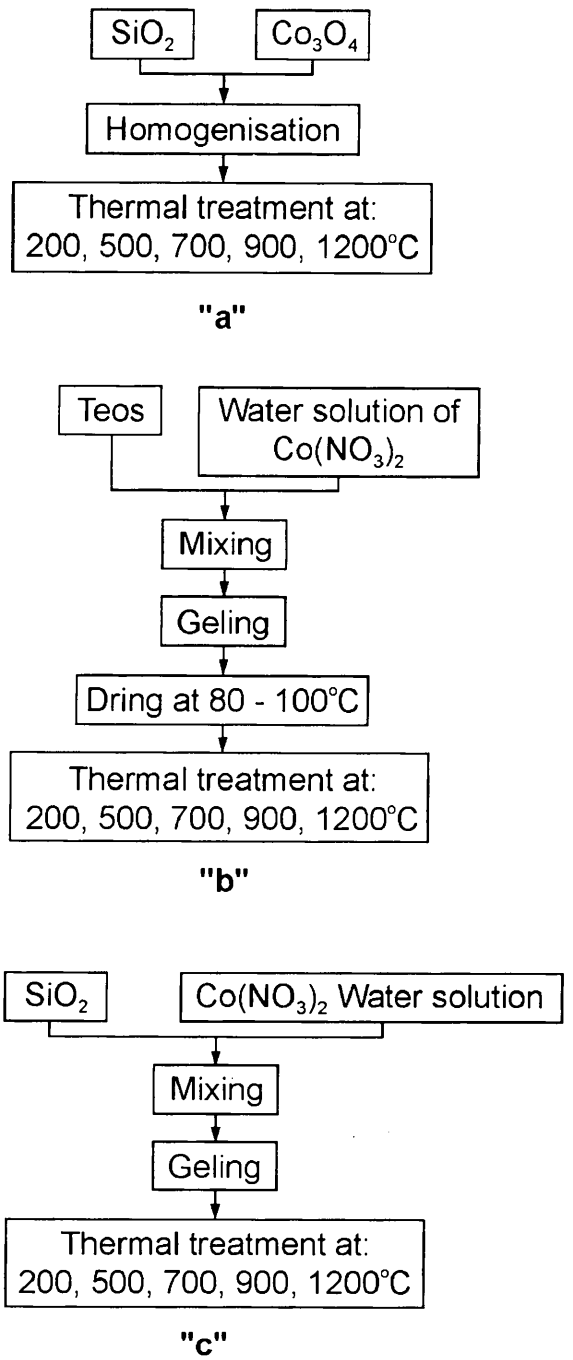



***Figure 1.*** *"a", "b", "c": Three variants for obtaining of cobaltous silicate*

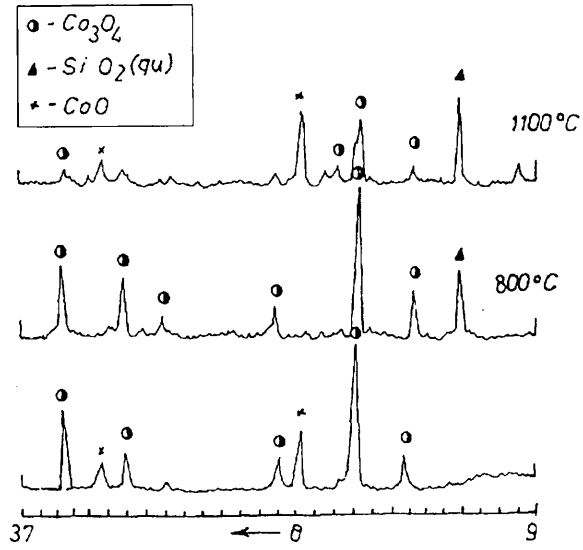



***Figura 2.*** *Diffractograms of the samples obtained by the conventional ceramic method version (a)*

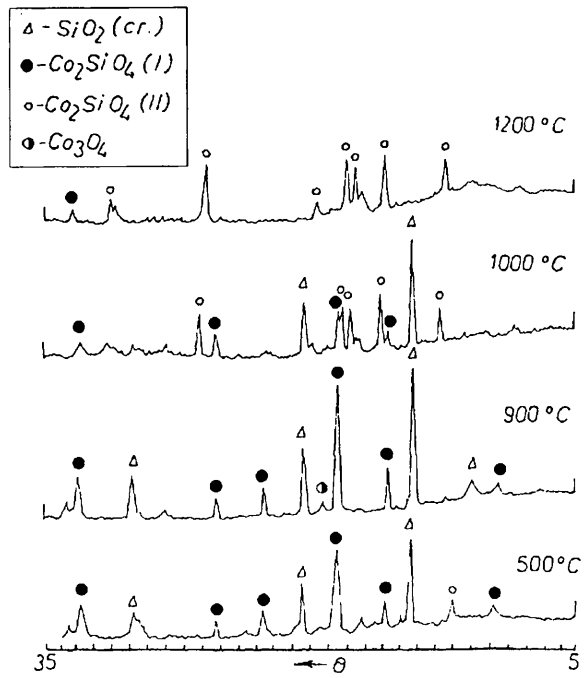



***Figura 3.*** *Diffractograms of the samples obtained dy sol-gel method version (b)*

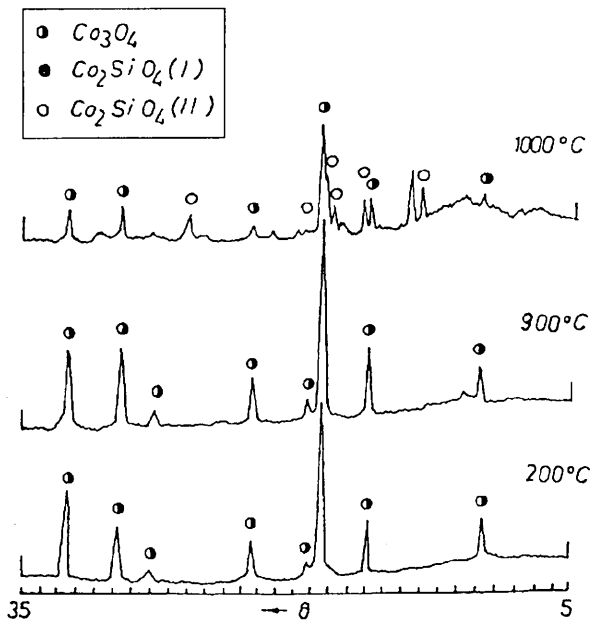



***Figura 4.*** *Diffractograms of the samples obtained by sol-gel method version (c)*

$$Co_3O_4 + SiO_2\ (qu) \longrightarrow Co_3O_4 + SiO_2\ (qu) \longrightarrow CoO + Co_3O_4 + SiO_2\ (qu)$$

$$TEOS + Co(NO_3)_2\ (qu) \longrightarrow AMORPHOUS \longrightarrow SiO_2(cr) + Co_2SiO_4(I) + Co_3O_4$$

$$\longrightarrow Co_2SiO_4(II) + Co_2SiO_4(I) + SiO_2\ (cr) \longrightarrow Co_2SiO_4(II)$$

$$SOL\text{-}SiO_2 + Co(NO_3)_2 \longrightarrow Co(NO_3)_2 \longrightarrow Co_3O_4 \longrightarrow Co_2SiO_4(II) + Co_3O_4 + SiO_2\ (qu)$$

***Figura 5.*** *The phaseforming mechanism related to the temperature increasing by the three systhesis versions*

The DTA-grams of the gels obtained by "b" and "c" method versions are shown in FIG.6. Mass losses are significant at low temperatures due to the dehydratation and destruction of organic substances in the samples. The reduction of $Co_3O_4$ to CoO is caused by the endoeffect in the temperature interval 780-940°C. It goes off at higher temperatures when the gels are obtained by the $SiO_2$-sol version-II method, which corresponds to the results of the X-ray analysis.

IR-analysis might be used for additional information about the phaseforming, as is well-known, and the different grade of the $SiO_4$ tetrahedronics polymerisation is related to the specific changes of the spectra. As is shown in FIG. 7 and FIG. 8, the basic bands might be interpreted as an oscillation of the $SiO_4$ tetrahedrons. Theoretically, the spectra of a single isolated $SiO_4$ tetrahedron should have four oscillations: $2F_2$, $E_d$, $A_1$. Due to the decreasing of the symmetry caused by the phaseforming, the degeneration is registered and the number of bands in the range 650-450 $cm^{-1}$ ($\nu_\delta$ $SiO_4$) increased [7, 8, 9, 10]. The formation of $Co_2SiO_n$ is approved by the increased intensity of the bands in the ranges 950-860 $cm^{-1}$ and 550-450 $cm^{-1}$. The band around 660 $cm^{-1}$ is characteristic for $Co_3O_4$ and its disappearance in the spectra shows that a chemical interaction runs off.

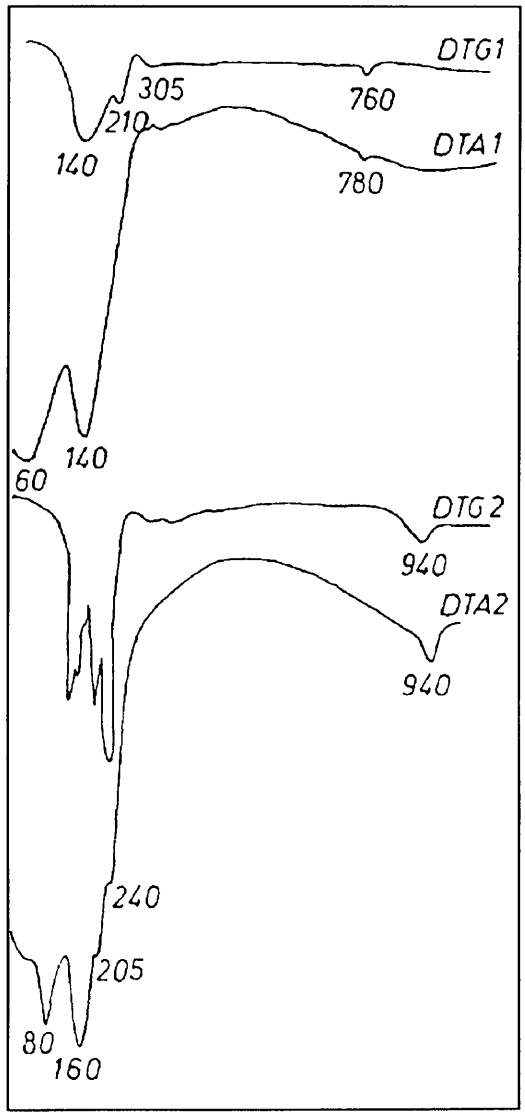
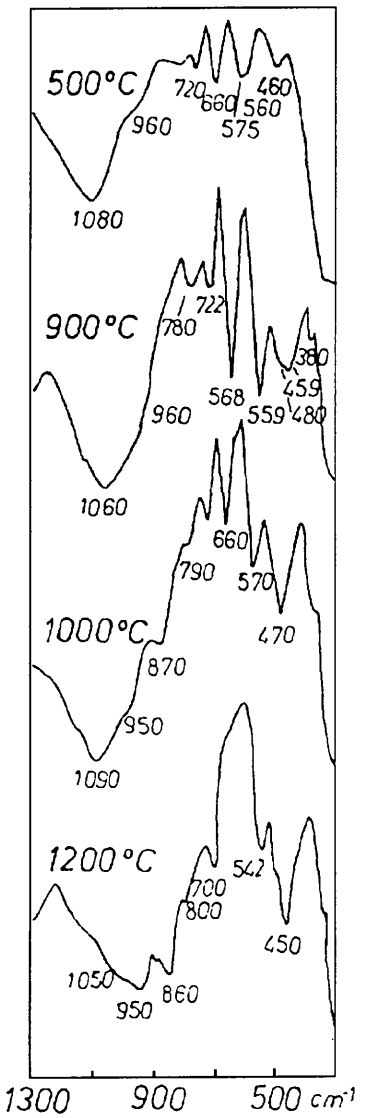



***Figura 6.*** *DTA curvs of gels obtained by sol-gel method (version b, c)*



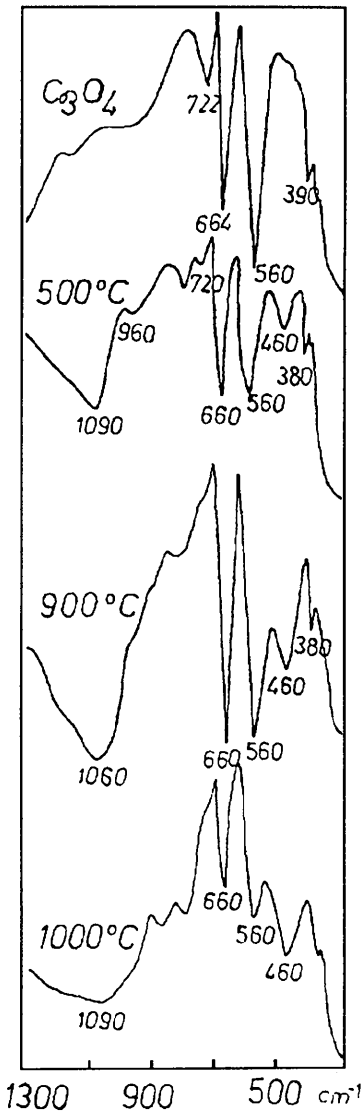




***Figura 7.*** *Ir-spectra of the gels obtained by sol-gel method (version b)*

***Figura 8.*** *Ir-spectra of the gels obtained by sol-gel method (version c)*

## CONCLUSION

As a result of the experimental research carried out, it might be confirmed that the type of the initial components and the way of obtaining the initial mixtures are of the essential significance for the grade of formation and transformation of the cobaltous silicate.

The obtaining of a monophase product at relatively low temperatures (under 1200°C) can be realized applying sol-gel technology when the $SiO_2$ is added in the form of TEOS.

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