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FORMATION OF CERAMIC PIGMENTS OF Sn–Cr TYPE. A STUDY USING THERMAL ANALYSIS METHODS

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ABSTRACT

Methods of thermal analysis (DTA and chemical analyses of pigments calcined at various temperatures) have been used for the determination of the temperatures of formation of the structures $CaSnO_3$, $CaSnSiO_5$ and $CaSiO_3$. $CaSnO_3$ and $CaSiO_3$ are formed at a temperature of 1100°C. In the system Sn–Ca–Si–Cr, $CaSnO_3$ is formed at first; when the temperature reaches 1300°C it reacts with silica to give $CaSnSiO_5$. The activation energies of formation of the host structures were evaluated.

INTRODUCTION

Pigments of chromium–tin type can produce various violet hues. They are prepared by calcining SnO_2 with $K_2Cr_2O_7$ or Cr_2O_3, usually with the addition of $CaCO_3$ and SiO_2 [1]. Thermostable structures of SnO_2, $CaSnO_3$ and $CaSnSiO_5$ are formed, which were confirmed by means of X-ray diffraction [2,3]. The mechanism of colour formation probably consists of Cr^{3+} ions entering into interstitial positions of the structures quoted [2–4]. This paper tries to complete the knowledge by the measurement of the temperature ranges of these structures and the kinetics of their formation.

METHODS

When preparing the pigment samples, the reaction mixtures were calcined at temperatures of 1000–1450°C in a KO II kiln (G.D.R.). The temperature was increased at a rate of 1.7 K min^{-1}. The formation of the individual structures was identified by means of X-ray diffractometry (HZG 4B, G.D.R.). Thermal analyses were carried out with a MOM-derivatograph (Q 1500). The colours were evaluated from reflectance curves (RFC-3, Opton).

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RESULTS AND CONCLUSIONS

Various reaction mixtures were prepared with the following molar compositions: $x\text{CaCO}_3 + y\text{SnO}_2 + z\text{SiO}_2 + w\text{K}_2\text{Cr}_2\text{O}_7$, $0 \leq x,\ y,\ z \leq 1$; $x+y+z=1$; $w = 3.3 \times 10^{-4}$ mol $K_2Cr_2O_7$ per g of mixture. The most important compositions were: $y=1$, $x=y=z=0.33$, $x=y=0.5$ and $x=z=0.5$, because they lead to the main types of pigments (Sn–Cr, Ca–Sn–Si–Cr, Ca–Si–Cr). The content of Cr was 3.4% by weight in all cases (also when Cr_2O_3 was used). The series without $K_2Cr_2O_7$ and with Cr_2O_3 were also prepared. The colour changes of some calcined samples are given in Fig. 1. The colour is given in the a^*, b^* coordinates (system CIE $L^*a^*b^*76$) and compared with that of pure SnO_2. The pigments of the Sn–Cr type are violet (lilac), Ca–Sn–Cr and Ca–Sn–Si–Cr are brownish-violet, and Ca–Si–Cr are green. The acid extraction (1 N acid) makes the violet hue of pigments deeper. The rate of formation of the coloured pigment can be represented by the colour difference ΔE (a distance from the centre of the L^*, a^*, b^* coordinates) and transformed into conversion of reaction, α, by relating it to the maximum value, $E_{\max}$. In this way kinetic curves were obtained, shown as (a) in Fig. 2. Their comparison indicates that pigments of Sn–Cr type need the highest temperature of calcination.

Similar curves were obtained from the values of Cr(VI), analytically determined in acid extracts of pigments (curves b in Fig. 2). The curves (c) correspond to Ca consumption in the reaction mixtures and so they reflect the formation of structures $CaSnO_3$, $CaSiO_3$ and $CaSnSiO_5$. These non-iso-

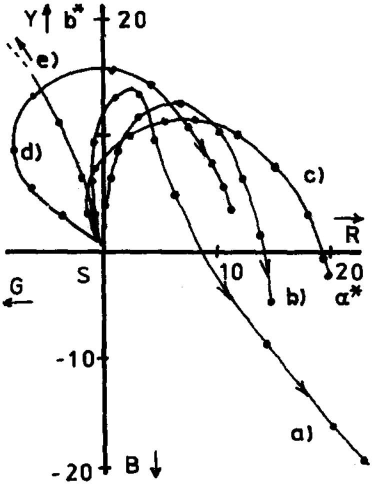

Fig. 1. Influence of the calcining temperature on colour. The points in the direction marked correspond to 50°C steps from 1000 to 1450°C. (a) Sn(Cr), (b) Ca–Sn–Si(Cr), (c) Ca–Sn(Cr), (d) 0.6Ca–0.2Sn–0.2Si(Cr), (e) Ca–Si(Cr). Sn, Ca and Si refer to the oxides, S = the reference SnO_2.

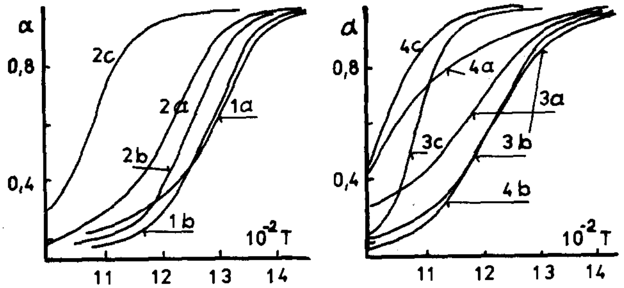

Fig. 2. Kinetic curves according to the colour (a), the content of Cr(VI) (b) and CaO (c) in calcinates. System of: Sn–Cr (1), Ca–Sn–Si–Cr (2), Ca–Sn–Cr (3), Ca–Si–Cr (4). Ca, Sn, Si refer to the oxides.

thermal kinetic curves were used for calculation of the activation energies, E_{exp} (Table 1).

The values obtained from the Cr(VI) analyses are slightly higher than those given from ΔE curves, but their sequence is the same. The highest E_{exp} value was found for the Sn–Cr system. The same E_{exp} values for systems B and C (within experimental error) show that CaO reacts in the same way in both cases, i.e., to $CaSnO_3$.

This fact is also confirmed by thermal analyses (Fig. 3). On these DTA curves the same exothermic peaks appear, near a temperature of 1100°C, as those on the thermograms for the $CaCO_3 + SnO_2$ mixture. The peak of silica transformation during cooling disappears when calcining the mixture above a temperature of 1300°C. This means that $CaSnO_3$ is formed at first in the system of the three oxides, and then it reacts with silica when a temperature of 1300°C is attained. The mixture $CaCO_3 + SiO_2$ also gives an exopeak at a slightly lower temperature than $CaCO_3 + SnO_2$. The formation of all these phases was confirmed by the X-ray method. If $K_2Cr_2O_7$ is also present in the reaction mixture, two endothermic peaks (400 and 670°C) appear on the DTA curves. The first peak corresponds to melting, the second one appears

TABLE 1

Activation energies E_{exp} obtained for curves a, b and c in Fig. 2 according to the relationship $\ln g(\alpha) - 2\ln T = a - b/T$ [a], $E_{exp} = bR - 2R\bar{T}$ [5]

System	E_{exp} (kJ mol^{-1}) for curve		
	a	b	c
Sn–Cr (A)	300	340	–
Ca–Sn–Cr (B)	150	180	260
Ca–Sn–Si–Cr (C)	220	250	250
Ca–Si–Cr	130 [b]	210	200

[a] The g(α) function for Jander's model (D2) was satisfactory.

[b] An estimate; the curve is not complete.

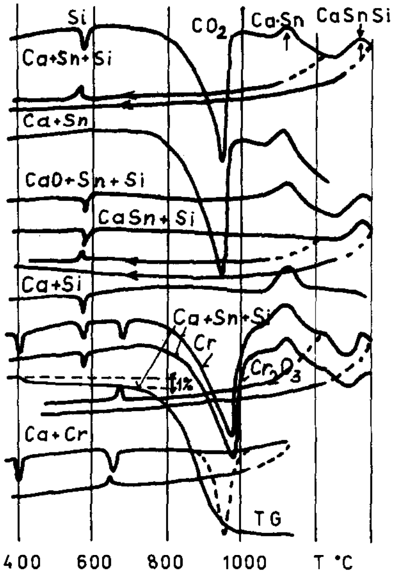

Fig. 3. Thermal analyses (DTA and TG). Ca, Sn, Si refer to the oxides, CaSn = $CaSnO_3$, CaSnSi = $CaSnSiO_5$, Cr = potassium dichromate.

when CaO or $CaCO_3$ is present. The 1% weight loss at temperatures above 400°C probably corresponds to the evaporation of the melted dichromate. Cr_2O_3 has the same effect as dichromate on the formation of these pigments.

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