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THERMAL PREPARATION OF GREEN-BROWN ZIRCON PIGMENTS

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Abstract

A new multi-component mineralizer is proposed which permits the synthesis of zircon pigments $Zr_{1-y-z}Mo_yCr_z^{IV}SiO_4 \cdot xCr_2O_3$ in an interesting green-brown hue.

Keywords: thermal preparation, zircon pigments

Introduction

Pigments based on the zirconium silicate formed during their thermal synthesis have the structure of zircon mineral. Most usually, they are prepared by calcination of mixtures of the basic starting oxides (ZrO_2 and SiO_2) together with a mineralizer and chromophores.

Experimental

The measurements were carried out with a Q-1500 derivatograph (MOM, Budapest). The basic starting oxides for use in the preparation of the mixtures for synthesis of the pigments were ZrO_2-7 (Goldschmidt) of 97.7% (w/w) purity, and SiO_2 from Austria [1]. Our new mineralizer [2] contains Na_2SiF_6, LiOH, MoO_3 (and NaCl).

Results and discussion

The TG curves of mixtures A and B (Fig. 1) show mass decreases corresponding to the release of water from LiOH (at about 100, 350–400 and 500°C) and its slow reactions with Na_2SiF_6 and with SiO_2 [Eqs (1)–(3)]. The reaction of formation of zirconium silicate commenced at a temperature (T_{Ri}) of 720–730°C in the mixture, the relatively sharp maximum (T_m) of this exothermic process being observed at 790°C. When MoO_3 was used in the starting mixture (C), the reaction was shifted to lower temperatures, its commencement and maximum then being at 640 and 700°C, respectively. The exothermic effect was

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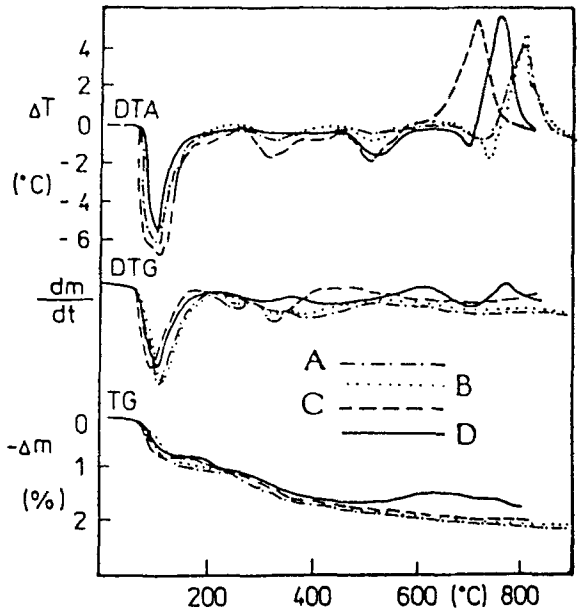

Fig. 1 Simultaneous TA curves of mixtures A–D Apparatus : Q–1500 derivatograph; rate of temperature increase: 10 deg·min^{-1}; sensitivity: TG 100 mg, standard: $\alpha - Al_2O_3$; atmosphere: air; platinum crucible with a lid. Mixtures/sample masses /g for TA: A = 0.80 ZrO_2 + 0.36 SiO_2 + 0.08 Na_2SiF_6 + 0.04 $LiOH{\cdot}H_2O$; B = A + 0.02 NaCl; C = B + 0.08 MoO_3; D = C + 0.14 Cr_2O_3

greater. The TG curve showed a slight mass decrease from 500°C; this is connected with a partial release of oxygen from MoO_3 (4). This oxygen, which is released in an active form, has distinct mineralization effects (in addition of halogens) [3, 4], due to its high electronegativity (5) (6). Therefore, the temperature of formation of zirconium silicate is decreased, the exothermicity ($-\Delta H$) increases, and the silicate content determined in a sample after completion of TA (Table 1) increases. Thermal analysis of mixture D revealed that the addition of a chromophore (Cr_2O_3) shifts the exothermic effect of formation of the pigment towards higher temperatures; addition of the chromophore also slightly lowers both the exothermicity of the process and the yield (Table 1).

$$LiOH{\cdot}H_2O = LiOH + H_2O \quad (1)$$

$$6LiOH + Na_2SiF_6 = (M_2SiO_3) + 6MF + 3H_2O \quad (2)$$

$$2LiOH + SiO_2 = (Li_2SiO_3) + H_2O \quad (3)$$

$$MoO_3 = MoO_2 + 1/2O_2 \quad (4)$$

$$4MF_{(l)} + 3SiO_{2(s)} = 2(M_2SiO_3)_{(l)} + SiF_{4(g)} \quad (5)$$

$$SiF_{4(g)} + ZrO_{2(s)} + O_2 = ZrSiO_{4(s)} + 2F_2 \quad (6)$$

$$(M = Li, Na)$$

The mass slightly increases above 500°C (with a local maximum at 600°C), and then a slight decrease occurs. On pigment formation (above 695°C), the mass again begins to increase.

Table 1 Some quantities determined from TA

Mixture	T_{Ri}/°C	T_m/°C	$-\Delta H$/ kJ·mol^{-1}	Yield / %
A	720–730	790	12.6	61.8
B	730	790	13.8	64.2
C	640	700	20.6	82.6
D	695	740	19.2	78.5

Alkali present in the reaction mixture acts on the Cr_2O_3 grains and causes a partial entry of Cr into the liquid phase, where it is oxidized to some higher valency [5]. When the temperature increases, the oxygen is again slowly released until $ZrSiO_4$ formation occurs, when some of the Cr ions in the higher valency are incorporated into the zircon structure. This is demonstrated by a temporary mass increase. This reaction of coloured zircon pigment synthesis is thus shifted to higher temperatures. The conversion of Cr^{3+} to a higher valency consumes oxygen from the reaction mixture, and according to the mineralizing effect this appears negatively: the exothermicity and yield of the reaction decrease (6) (Table 1).

References

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Zusammenfassung — Es wird ein neuer Mehrkomponenten-Mineralisator vorgeschlagen, der die Synthese von Zirkonpigmenten $Zr_{1-y-z}Mo_y^{IV}Cr_z^{IV}SiO_4 \cdot xCr_2O_3$ in einem interessanten grünbraunen Farbton gestattet.