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Synthesis of Yellow Pigments from Zircon Mineral

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ABSTRACT

Zirconium silicate (zircon) pigments having a yellow colour have been prepared from zircon mineral as the starting raw material. The first stage involves decomposition of the zircon mineral with a waste mixture of NaOH and KOH. In the second stage, the pigments are synthesized by addition of praseodymium oxide as the chromophore. Optimum conditions for the synthesis of the pigments have been established, the properties of product have been evaluated, reasons for their colour hue are explained, and their applicability to ceramic glazes has been evaluated.

INTRODUCTION

Our previous papers[1–5] describe a method of synthesis for a relatively feasible production of some zircon pigments from the cheap starting zircon raw material, viz. zircon mineral (a general procedure,[1] and preparation of blue–green,[2] pink–violet,[3] blue–violet[4] and brown–green pigments[5]). In the first step the zircon mineral is decomposed by alkali fusion with a mixture of NaOH and KOH (molar ratio of 1:1) available as a waste material from the machine industry. In an intermediate stage of modification of the decomposition products, the halogenide component is added, followed by the chromophore. In the second step, the modified decomposition products are calcinated to give the zirconium silicate pigments. The method of preparation of these pigments is simple, technologically feasible, and utilizes both the silicate and the zirconium(IV) components of the starting zircon

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mineral, giving pigments of desirable quality and in sufficient yield. The use of praseodymium oxide as chromophore made it possible to synthesize zirconium silicate pigments of yellow hues[6] and this process is described in the present communication.

EXPERIMENTAL

The starting material used was a zircon mineral of Australian origin (content 96% $ZrSiO_4$, finely ground, with prevailing grain size of 1–4 μm).[7] The basic mixture for the preparation of the pigments was formed from 10 parts of this mineral decomposed with 4 parts of the NaOH–KOH mixture at 750–800°C for 1·5–2 h. After cooling, 8·6 parts of 20% HF and 8·4 parts of 15% HCl were added.[1,2] The yellow pigments were synthesized after the addition of the chromophore, i.e. praseodymium oxide, Pr_6O_{11}. On the basis of preliminary experiments, the chromophore was applied in an amount corresponding to 1·17 parts of Pr_6O_{11}.

The most suitable conditions (temperatures and calcination times) for production of the pigments by calcination of the mixture were determined, and by varying the chromophore content, the hue of the resultant pigments was also changed. The pigments were applied to two types of ceramic glazes, viz. a medium-temperature (glazing temperature 1050°C) and a high-temperature glaze (1300°C).[8]

After the calcinations, the calcinates were extracted with 15% HCl (10 min boiling) and with respect to the degree of conversion to the pigment (using the method developed by us[9]) and to the colour hue. The colour intensity was measured as reflectance in the visible region, with both the powdered pigments and glazes containing 10% (w/w) of pigment using a Spekol 10 with a remission adaptor R45/0 (Zeiss Jena, GDR). The chemical nature and reasons for the colour of the pigments were concluded on the basis of X-ray diffraction and electron microscopy studies.

RESULTS AND DISCUSSION

In the temperature interval from 650 to 1100°C (calcination time 1 h, increase in temperature 20°C min^{-1}, holding time 1 h) the mixture was calcinated; the chromophore content was 1·17 parts of Pr_6O_{11} (denoted as Mixture VII in Table 1). Figure 1(A) shows the degree of conversion of the calcinate into the pigment at various temperatures. It can be seen that, for the yellow pigment, a sufficient degree of conversion is attained above 800°C and a steady-state (maximum) degree of conversion above 900–1000°C.

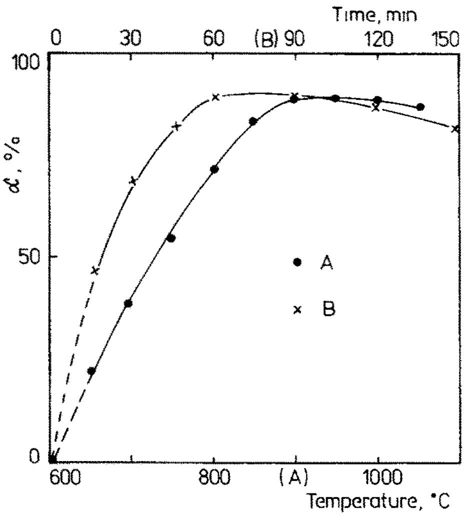


Fig. 1. Dependence of the degree of conversion (α) of the starting mixture (VII; see Table 1) to the yellow pigment, (A) on the calcination temperature (for calcination time 1 h; ●) and (B) on the calcination time (for calcination temperature 900°C; ×).

At the temperature chosen (900°C) the degree of conversion of the calcinate into the pigment as a function of the calcination time was assessed [Fig. 1(B)]. It was found that the maximum conversion was achieved after 60–90 min calcination, and that further prolongation resulted in a decrease in the degree of conversion. This is due to too high an alkali content in the calcinated mixture; after the mildly exothermic reaction of the pigment synthesis is completed, the alkali decomposes the product.

From Fig. 2 it can be seen that the pigments and the glazes made therewith have yellow colour hues, the most suitable temperature for the production of the yellow pigment being 900°C. Also, the colour intensity of the pigments prepared at 900°C and at various times of calcination, and that of the glazes coloured therewith, show that a calcination time of 60–90 min represents the optimum at the temperatures mentioned (Fig. 3).

The formation of zirconium(IV) silicate as the basis of yellow pigment can be represented by eqns (1)–(6). The starting decomposition products are *de facto* alkali silicozirconates [eqn (1)],[10] after wetting with acids they can be presumed to decompose, to a certain extent, to give the individual zirconium(IV) and silicon(IV) components [eqn (2)] which are dehydrated in the initial part of the calcination [eqn (3)].

$$M_2ZrSiO_5 + 2HX = (H_2ZrSiO_5) + 2MX \tag{1}$$

$$H_2ZrSiO_5 + H_2O = H_2ZrO_3 + H_2SiO_3 \tag{2}$$

$$H_2ZrO_3 + H_2SiO_3 = ZrO_2 + SiO_2 + 2H_2O \tag{3}$$

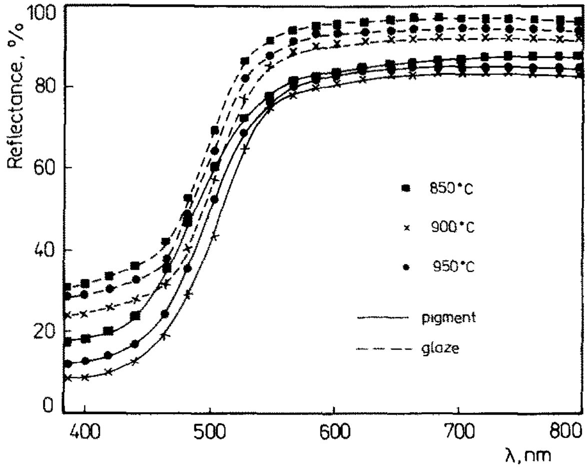


Fig. 2. Colour hue of the yellow pigments (——) synthesized from Mixture VII at temperatures of 850°C (■), 900°C (×) and 950°C (●) (for 1 h) and colour hue of high-temperature glaze (temperature of glazing 1300°C; – – –) with 10% (w/w) pigments.

At higher calcination temperatures, the mineralizer of the alkali halogenide type [which has formed in the reaction mixture of eqn(1)] begins to operate. It attacks the grains of both the oxides and converts especially the silicate component into a transportable phase, either an alkali silicate melt or gaseous SiX_4 [eqn (4)], which reacts with the zirconium(IV) component to give zirconium(IV) silicate [eqns (5) and (6)].

$$4MX + nSiO_2 = (n - 3)SiO_2 + 2(M_2SiO_3) + SiX_4 \quad (4)$$

$$(M_2SiO_3) + ZrO_2 = ZrSiO_4 + (M_2O) \quad (5)$$

$$ZrO_2 + SiX_4 + O_2 = ZrSiO_4 + 2X_2 \quad (6)$$

$$(M = Na, K; X = F, Cl)$$

The last reaction [eqn (6)] producing the halogens is very important; because of their high electronegativity, the halogens are shielding the large mutual repulsive forces of the zirconium(IV) and silicon(IV) ions, thus enabling their mutual approach and reaction.[11,12,13] Similar favourable effects are also observed with oxygen, which has an electronegativity between fluorine and chlorine.[14,15] Therefore, a change in its concentration in the calcinated mixture (e.g. due to the reaction of chromophore) is also reflected in the conditions of the pigment synthesis. In contrast to previous findings,[2] however, the oxygen concentration in this the present case is affected not positively but negatively by the chromophore. The synthesis of the yellow pigment is shifted by 100°C to higher temperatures compared with that of the synthesis of pure $ZrSiO_4$ (without the chromophore[1]). The praseodymium present in its trivalent state [caused by calcination at 260–300°C,[16]

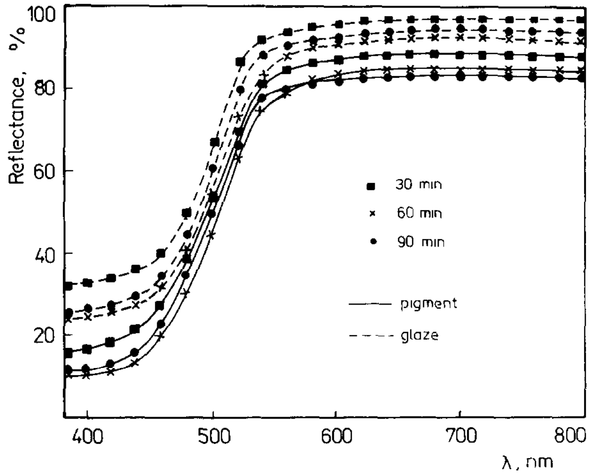


Fig. 3. Colour hue of the yellow pigments (——) synthesized from Mixture VII at calcination times of 30 min (■), 60 min (×) and 90 min (●) (temperature 900°C) and colour hue of high-temperature glaze (temperature of glazing 1300°C; ---) with 10% (w/w) pigments.

see eqn (7)] in the melt phase of the mixture must be transformed into the tetravalent state at the moment of formation of the pigment. Only in this way can it be incorporated into the zircon structure of the pigment in the form of substitution uncharged defects in place of zirconium (Pr_{Zr}^{x}); these defects are responsible for the yellow hue of the pigment. However, in this way oxygen is exhausted from the mixture [eqns (8) and (9)].

$$Pr_6O_{11} = 3Pr_2O_3 + O_2 \tag{7}$$

$$SiX_4 + (1-x)ZrO_2 + \left(\frac{x}{2}\right)Pr_2O_3 + \left(1+\frac{x}{4}\right)O_2 = Zr_{1-x}Pr_xSiO_4 + 2X_2 \tag{8}$$

$$(M_2SiO_3) + (1-x)ZrO_2 + \left(\frac{x}{2}\right)Pr_2O_3 + \left(\frac{x}{4}\right)O_2 = Zr_{1-x}Pr_xSiO_4 + M_2O \tag{9}$$

$$(M = Na, K; X = F, Cl)$$

Electron microscopy shows that the pigment is formed in 5–7 μm regular particles which are unfolded at their surface very well. X-Ray diffraction analysis confirmed that the microcrystals of both pigments correspond to a tetragonal space-centred system (the zircon structure); its calculated structural parameters are: $a_0 = 0{\cdot}660\,62$ nm, $c_0 = 0{\cdot}598\,33$ nm, and the volume of the elementary unit cell $V = 0{\cdot}261\,08$ nm^3. Hence the structural parameters are slightly higher than those of pure zirconium silicate synthesized on the same principles, but without chromophore.[1] The higher values of the structural parameters of the yellow pigment indicate the

TABLE 1

Content of Pr_6O_{11} in the Mixture for the Preparation of Yellow Pigments

Mixture no.	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*
Pr_6O_{11} content (parts)	0·13	0·43	0·75	0·80	0·94	1·125	1·17	1·25	1·50	1·67

incorporation of a limited amount of praseodymium ions in the tetravalent state (and of greater ionic radius) into the $ZrSiO_4$ structure; these ions replace the zirconium ions (of smaller ionic radius) as substitution uncharged defects.[15]

The influence of the content of chromophore in the mixture on the colour hues of the pigment was investigated. The proportion of chromophore in the decomposition products which were prepared by alkali melting of zircon with the waste NaOH–KOH mixture and wetted with HF and HCl (i.e. using the same procedure as that described above for a content of 1·17 parts Pr_6O_{11}) was changed within the range 0·13–1·67 parts (see Table 1). The pigments were synthesized at 900°C for 60 min. The colour hues of the pigments, expressed by the reflectance in the visible, are shown in Fig. 4. The pigments were of various intense yellow hues and the most satisfactory colour hues were obtained when the chromophore content corresponded to mixtures VI and VII (i.e. with 1·125 and 1·17 parts Pr_6O_{11} corresponding to approximately about 7% in the dry mixture). Increase in chromophore content over these limits caused no deepening of the yellow colour.

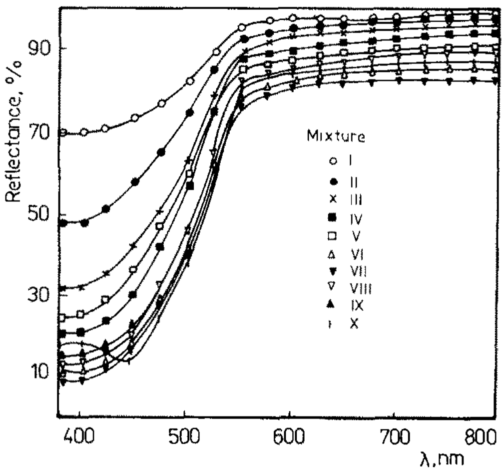
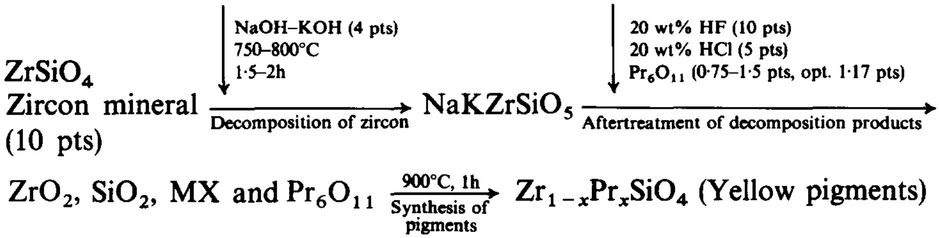


Fig. 4. Effect of the content of the chromophore Pr_6O_{11} in the mixtures I–X (see Table 1) on the colour hue of the yellow pigments (calcination temperature 900°C for 1 h).

CONCLUSION

According to the process[6] proposed in this work, the synthesis of yellow zirconium silicate pigments of mineral zircon can be described by Scheme 1. The pigments are characterized by an intense colour and high thermal stability and can be applied to all kinds of ceramic glazes.



$$\begin{array}{l}\mathrm{ZrSiO_4}\\ \text{Zircon mineral}\\ \text{(10 pts)}\end{array} \xrightarrow[\text{Decomposition of zircon}]{\begin{array}{l}\text{NaOH–KOH (4 pts)}\\ \text{750–800°C}\\ \text{1·5–2h}\end{array}} \mathrm{NaKZrSiO_5} \xrightarrow[\text{Aftertreatment of decomposition products}]{\begin{array}{l}\text{20 wt\% HF (10 pts)}\\ \text{20 wt\% HCl (5 pts)}\\ \mathrm{Pr_6O_{11}}\ \text{(0·75–1·5 pts, opt. 1·17 pts)}\end{array}}$$

$$\mathrm{ZrO_2,\ SiO_2,\ MX\ and\ Pr_6O_{11}} \xrightarrow[\text{Synthesis of pigments}]{\text{900°C, 1h}} \mathrm{Zr_{1-x}Pr_xSiO_4}\ \text{(Yellow pigments)}$$

(M = Na, K; X = F, Cl; pts = weight part)

Scheme 1

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