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Synthesis of a Pink–Violet Zirconium Silicate Pigment from Zircon Mineral

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ABSTRACT

A new procedure for the preparation of pink–violet zirconium silicate pigments from zircon mineral is described. The method makes use of a waste KOH/NaOH mixture for decomposition of the zircon mineral and is very economical from the point of view of consumption of energy and raw materials. It does not necessitate any treatment of the decomposition products by extraction or precipitation, and the alkali ions present therein participate in the pigment synthesis as mineralizer components.

INTRODUCTION

A number of procedures exist for the synthesis of zirconium silicate (zircon) pigments starting from the zircon mineral as the raw material. In the first step, however, it is necessary to carry out decomposition of zircon; the intermediate step usually involves a treatment of the decomposition products, and the second step consists of the pigment synthesis proper, eqn (1).

Zircon mineral is a highly stable compound, both chemically and thermally, and its decomposition is therefore exacting with respect to both energy consumption and raw materials. The treatment of decomposition products, with the object of making them suitable as starting mixtures for the pigment synthesis, can be, from a technological point of view, the most exacting operation of the whole procedure. Therefore, the most simple

$$\underset{\text{(Zircon mineral)}}{\mathrm{ZrSiO_4}} \xrightarrow[\text{(}T\text{, decomposition medium)}]{\text{decomposition}} \text{Decomposition products} \xrightarrow[\text{(extraction, precipitation, drying, etc)}]{\text{aftertreatment}}$$

$$\begin{array}{l}\mathrm{Zr^{IV}}\text{ component}\\ \mathrm{Si^{IV}}\text{ component}\\ \text{(possible}\\ \text{separation)}\end{array} \xrightarrow[\text{(}T\text{,chromophore, mineralizer, }\mathrm{SiO_2}\text{ if necessary)}]{\text{pigment synthesis}} \mathrm{ZrSiO_4}\text{ pigment} \qquad (1)$$

treatment of the decomposition products is needed in cases when zircon has been decomposed only by application of high temperatures or by the action of plasma.[1] In such cases the decomposition products represent a practically equimolar mixture of ZrO_2 and SiO_2, so that after addition of the chromophore and mineralizers it is possible to prepare the pigment directly.

The above method of decomposition of zircon, however, is characterized by high energy consumption, a drawback which at present predominates over its simplicity. Therefore, it is more convenient to adopt methods of decomposition of zircon based on its fusion with alkali and use of temperatures currently attainable in the ceramic industry. The majority of procedures make use of sodium carbonate[2-4] for the decomposition, this alkali being relatively cheap and effective. The decomposition temperature, however, is relatively high and the treatment of decomposition products is usually exacting. Other procedures[5] are even more exacting with respect to the operations of treatment of the decomposition product (after alkaline fusion), because they transform the decomposition products to ZrO_2, the silicate component not being used, hence SiO_2 must be added before the pigment synthesis proper.

The object of our investigation was to find an economical and readily available alkaline medium which would be able to decompose the zircon mineral effectively at temperatures more favourable than those needed for decomposition with soda. Another aim was to simplify, as much as possible, the operations of the aftertreatment of the decomposition products and to utilize the alkali ions from the decomposition products in the pigment synthesis proper. (During the synthesis these ions act as one component of the mineralizer, i.e. M in MX of the alkali halogenides; see eqn (4)). For this purpose, a mixture of NaOH/KOH (molar ratio NaOH/KOH = 1)[6] proved to be the best. The NaOH/KOH mixture combines the good decomposition effects of both the hydroxides; the NaOH component lowers the decomposition temperature, and the KOH component increases the decomposition efficiency. For this purpose, a waste medium (i.e. a mixture of NaOH/KOH) which is used as a hardening temperature bath in the engineering industry, proved to be very satisfactory.

EXPERIMENTAL

Zircon mineral (of Australian origin) was used as the starting raw material. We initially evaluated some of its physical properties and determined its $ZrSiO_4$ content by a method developed in our laboratory:[7] 96% (w/w) $ZrSiO_4$; particle size 1–4 μm (>90% by weight).

The basis of the starting mixture for the synthesis of zircon pigments was formed by the decomposition products obtained by decomposition of the Australian zircon with an NaOH/KOH mixture (a waste hardening bath from the machine industry was used) at 750–800°C for 1·5–2 h.[6] By weight this represents 4 parts of hydroxide per 10 parts of zircon. The decomposition products are (after the alkaline fusion is finished) practically always in a loose powdery form (decomposition set about 90%).

Owing to the amount of alkaline hydroxides used in the decomposition; the decomposition products are represented by $NaKZrSiO_5$ [eqn (2)]:

$$ZrSiO_4 + NaOH + KOH = NaKZrSiO_5 \qquad (2)$$

For incorporating halides (as second components of the mineralizer) into the mixture we used hydrofluoric and hydrochloric acids (as a source of F^- and Cl^-). It can be assumed that the reaction (3) is partially realized. Therefore the most convenient amounts of these acids were determined.

$$NaKZrSiO_5 + 2HX = ZrO_2 + SiO_2 + NaX + KX + H_2O \ (X = F, Cl) \qquad (3)$$

Iron compounds (acting like chromophores) are used for the preparation of zircon pigments with pink hues.[8] For this work the following compounds were used in an amount of 1 part relative to the $NaKZrSiO_5$: FeOOH, Fe_2O_3, $FeSO_4.7H_2O$, $Fe(NO_3)_3.9H_2O$, $FeCl_2.4H_2O$ and $(NH_4)_2Fe(SO_4)_2.7H_2O$.

The optimum conditions for the synthesis of the pigments, i.e. the temperature of synthesis and necessary time of calcination at this temperature, were determined for the proposed mixture compositions together with the appropriate chromophore. At the same time the degree of the conversion of the calcinate to pigment was checked by the method developed by us.[9] After determination of the optimum conditions of the synthesis, the most favourable content of the chromophore in the mixture was determined. The calcinates (after cooling) were extracted with hydrochloric acid (15 mol % concentration, 10 min boiling). After extraction, the solid phase was separated by filtration and dried. The pigments thus obtained were evaluated in several ways. Structural parameters were determined by X-ray diffraction (HZG-2, GDR) and electron microscopy. The origin of the colour of the pigments is also discussed. The size and regularity of the pigment particles are also assessed.

The hue of the pigments was evaluated by spectral reflectance measurements in the visible region using a Spekol 10 apparatus with the R 45/0 reflectance adaptor (Zeiss, Jena). The pigments prepared were applied to ceramic glazes at medium and high temperatures (glazing temperatures of 1050 and 1300°C, respectively). The final glazes were evaluated with regard to their hues and the mechanical evenness of their surfaces.

RESULTS AND DISCUSSION

As a result of our earlier work[6] and some preliminary experiments, the amount of halogen-hydride acids which was convenient to spray the decomposition products was determined. These corresponded to 2 parts of pure HF and 1 part of pure HCl. The use of 20% acid was shown to be convenient from the point of view of good binding of halogen hydroxides in the mixture of the decomposition products (i.e. 10 parts of 20% HF and 5 parts of 20% HCl were used to spray the decomposition products). Of the various iron compounds studied (FeOOH, Fe_2O_3, $FeSO_4 . 7H_2O$, $Fe(NO_3)_2 . 9H_2O$, $(NH_4)_2Fe(SO_4)_2 . 7H_2O$ and $FeCl_2 . 4H_2O$), iron dichloride $FeCl_2 . 4H_2O$ (a waste product of steel pickling) was shown to be the most convenient. Its chloride component functions in the synthesis of the pigment as a constituent of the second halogen component of the mineralizer and the use of this material gave the most intensely coloured pigment (pink–violet hues).

The starting mixture obtained by decomposition of 10 parts of zircon (mixture of alkali hydroxides, i.e. 2 parts of NaOH and 3 parts of KOH at 750°C for 2 h) was sprayed with 10 parts of 20% HF and 5 parts of HCl after cooling. It had an optimum composition and was heated at various temperatures within the range 650–1100°C (for 120 min) after adding 2 parts of $FeCl_2 . 4H_2O$.

The reaction shown in eqn (4)

$$4MX_{(l)} + nSiO_{2(s)} = (n-3)SiO_{2(s)} + 2(M_2SiO_3)_{(l)} + SiX_{4(g)} \tag{4}$$

sets the course of the calcination of the mixture of the zirconate and the siliceous parts formed by reaction (3). The iron chromophore also undergoes reaction with SiO_2 [eqn (5)] and the formation of α-Fe_2O_3 was confirmed by X-ray diffraction analysis. The major part of the zirconium silicate arises by transport of the siliceous part in the form of tetrahalide [eqns (6) and (7)]. A simultaneous reaction produces α-Fe_2O_3 [eqn (5)] whose particles are immediately incorporated into the microcrystals of the $ZrSiO_4$ thus formed to give the pink pigment $(ZrSiO_4)_{1-y} . yFe_2O_3$ [eqn (7)].

$$2FeCl_2 + SiO_2 + 1/2O_2 = SiX_4 + Fe_2O_3 \tag{5}$$

$$SiX_{4(g)} + ZrO_{2(s)} + O_2 = ZrSiO_{4(s)} + 2X_{2(g)} \qquad (6)$$

$$(1-y)SiX_4 + 2yFeX_2 + (1-y)ZrO_2 + (1+0{\cdot}5y)O_2 = (ZrSiO_4)_{1-y}.yFe_2O_3 + 2yX_2 \qquad (7)$$

Because of a transfer of the siliceous part by the liquid phase [eqn (8)] obtained by reaction (4), zirconium silicate is also formed. The pink hue of the pigment [eqn (9)] arises by the same mechanism.

$$(M_2SiO_3)_{(l)} + ZrO_{2(s)} = ZrSiO_{4(s)} + (M_2O)_{(l)} \qquad (8)$$

$$(1-y)(M_2SiO_3) + (1-y)ZrO_2 + 2yFeX_2 + 1{\cdot}5yO_2 = (ZrSiO_4)_{1-y}.yFe_2O_3 + (1-y)M_2O + 2yX_2 \qquad (9)$$

For the formation of the violet hue of the pigment, the following explanation can be proposed. The large amount of alkali ions present in the reaction mixture in the melting phase allows the conversion of a small part of the iron ions to the high-valency form (Fe^{VI}).[10] At the same time zirconium silicate is formed. These ions are like substituted positively charged defects with a tetrahedral structure. They are the origin of the violet part of the pigment colour and their higher formal positive charge is compensated by the small amount of alkali-metal ions occurring on the negatively charged defects in place of zirconium.

$$(M_2SiO_3) + (1-x)ZrO_2 + 0{\cdot}6xFeX_2 + 0{\cdot}6xO_2 = Zr_{1-x}M^{I}_{0{\cdot}4x}Fe^{VI}_{0{\cdot}6x}SiO_4 + (1-0{\cdot}8x)M_2O + 1{\cdot}2xMX \qquad (10)$$

Reactions (7) (9) and (10) proceed simultaneously and the pink–violet colour of the pigment is the result of these reactions. Its common formula can be written as $(Zr_{1-x}M^{I}_{0{\cdot}4x}Fe^{VI}_{0{\cdot}6x}SiO_4)_{1-y}.y\alpha\text{-}Fe_2O_3$.

As is shown in Fig. 1, curve A, a sufficient degree of conversion is reached at a temperature of 750°C. An almost constant and maximum degree of conversion (above 82%) is reached at 800°C and above. An interesting observation was made by examination of the conversion degree at 850°C for various calcination times (Fig. 1, curve B). It was found that maximum conversion was achieved after 90 min calcination, and more prolonged times (especially above 120 min) resulted in a decrease of the conversion degree. The reason for this is too high an alkali content in the mixture calcinated. After the mildly exothermic reaction of the pigment synthesis is finished, the alkali decomposes the product (acting in a similar way to an alkaline fusion). For the synthesis proper of the pink–violet pigment, therefore, a calcination temperature of 800–850°C and a reaction time of about 1·5 h were chosen.

The hues of the pigments which were prepared under these conditions and the hues of middle-temperature glaze (temperature of glazing 1050°C) and

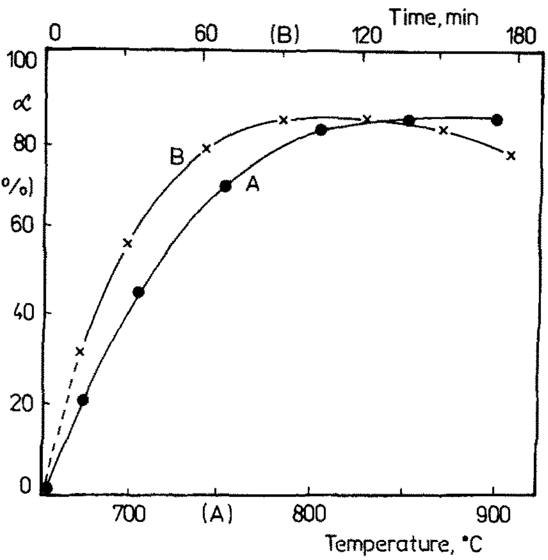

Fig. 1. Dependence of the conversion degree of the starting mixture to the pink–violet pigment on the calcination temperature (A, calcination time 120 min) and on the calcination time (B, calcination temperature 850°C).

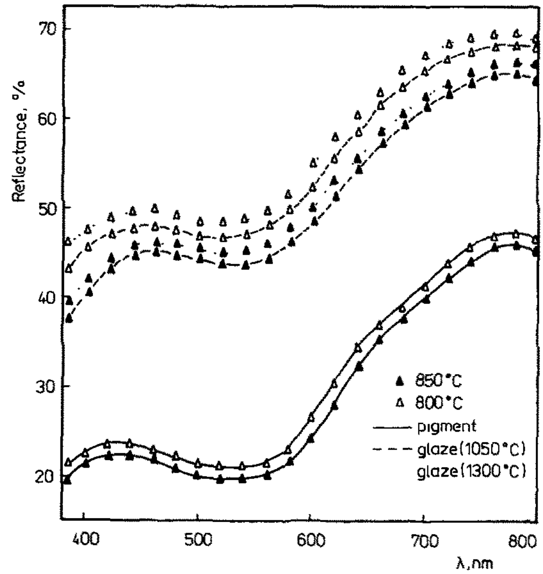

Fig. 2. The hue of the pink–violet pigments (——), synthesized at 850°C (▲) or 800°C (△) (time 1·5 h), and the colour hue of middle-temperature glaze (temperature of glazing 1050°C; – – –) and high-temperature glaze (1300°C; · · ·) with 10% pigments.

high-temperature glaze (1300°C) after the application of 10% pigment are shown in Fig. 2 and they confirm the pink–violet hue.

Electron microscopy showed that the pigment is formed by 5-μm regular particles which are unfolded on their surface very well. X-ray diffraction analysis showed that the microcrystals of the pigment were in a tetrahedral spatially centred system (i.e. a zircon structure). The structure parameters, $a_0 = 0{\cdot}66013$ nm, and $c_0 = 0{\cdot}59785$ nm, which were calculated on the basis, are a little lower than in pure zirconium silicate synthesized by the same method but without a chromophore.[6] This confirms the incorporation of a limited amount of iron ions of higher valency and of smaller ionic radius into the structure of the zirconium silicate. They are like substituted positively charged defects in place of zirconium ions, which have greater ionic radius.[11] Their incorporation is compensated for by the presence of larger ions of the alkali metals (Na) and is indicated by the decrease in the values of the structure parameters. Under electroneutrality conditions, the number of sodium ions which enter into structure of $ZrSiO_4$ is about halved. The sodium ions are not much larger than the zirconium ions which they replace, but the iron ions of higher valency are smaller in comparison. Distinguishable diffraction lines which could be related to α-Fe_2O_3 were also apparent. Although the electron microscopy studies did not show the presence of particles other than microcrystals of silicate, it confirmed that the particles of α-Fe_2O_3 can exist only as inclusions enclosed in the microcrystals of the pigment. These results agree with the suggested origin of the colour of this pink–violet zircon pigment, the colour being based on a combination of defect and inclusion principles (see the summary general formula of the pigment in Scheme (11)).

The influence of the content of the iron chromophore $FeCl_2 . 4H_2O$ in the mixture on the hue of the pigment was also evident. The portion of chromophore in the breakdown products which were prepared by alkali fusion of zircon with the NaOH/KOH mixture and sprayed with HF and HCl (i.e. the same process as was used with the mixture containing 1 part of $FeCl_2 . 4H_2O$) was varied over the range 0·5 to 6 parts (see Table 1). The pigments were synthesized at a temperature of 850°C over a period of 1·5 h. The hues of the pigments thus obtained were assessed by their reflectance in

TABLE 1

The Content of $FeCl_2 . 4H_2O$ in the Mixture for the Preparation of Pink–Violet Pigment

Mixture no.	*I*	*II*	*III*	*IV*	*V*	*VI*
Content of $FeCl_2 . 4H_2O$ (parts)	0·5	1	2	3	4	6

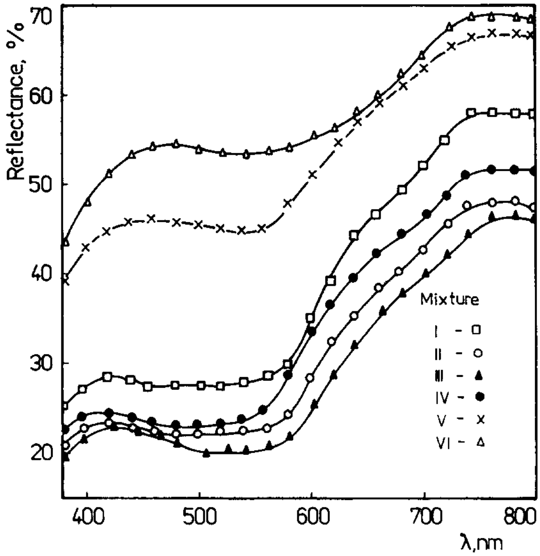

Fig. 3. Effect of the content of $FeCl_2 . 4H_2O$ in the mixtures I–VI (see Table 1) on the hue of the pink–violet pigment (calcination conditions: 850°C for 1·5 h).

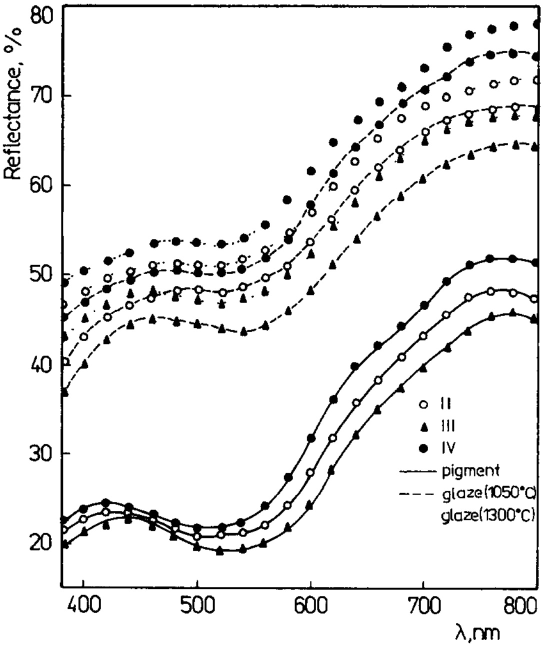

Fig. 4. The hue of the pink–violet pigments (——) synthesized (850°C, 1·5 h) from the mixture II (○), III (▲), IV (●) (see Table 1), and the hue of middle-temperature glaze (glazing temperature 1050°C; ---) and high-temperature glaze (1300°C; ···) with 10% pigments.

the visible range of spectrum and these values are shown in Fig. 3. For a pink–violet hue, mixtures III or II (i.e. with 2 and 1 parts of $FeCl_2 . 4H_2O$ and corresponding to approximately 16 and 8% respectively of iron chromophore in the mixture) were the most suitable. The hues of the middle-temperature and/or high-temperature glazes with 10% pigment (see Fig. 4) confirmed the very good thermal stability of the pigments. The dye glazes were a pink–violet hue.

CONCLUSION

According to the process[12] proposed in this work, the synthesis of pink–violet zirconium silicate pigments of mineral zircon can be described by the scheme [reactions (11)].

$$\underset{\substack{\text{Zircon mineral}\\ (10\ \text{pw})}}{ZrSiO_4} \xrightarrow[\text{decomposition of zircon}]{\substack{\text{NaOH/KOH (4 pw*)}\\ 750\text{–}800^{\circ}C\\ 1{\cdot}5\text{–}2\ h}} NaKZrSiO_5 \xrightarrow[\substack{\text{aftertreatment of}\\ \text{decomposition products}}]{\substack{20\ \text{wt\% HF (10 pw)}\\ 20\ \text{wt\% HCl (5 pw)}\\ FeCl_2 . 4H_2O\ (1\text{–}2\ \text{pw})}}$$

$$\underset{(M = Na,\ K;\ X = F,\ Cl)}{ZrO_2,\ SiO_2,\ MX,\ FeCl_2} \xrightarrow[\text{synthesis of pigment}]{800\text{–}850^{\circ}C,\ 1{\cdot}5\ h}$$

$$\underset{\text{Pink–violet pigment } (y \gg x)}{(Zr_{1-x}M^{I}_{0{\cdot}4x}Fe^{VI}_{0{\cdot}6x}SiO_4)_{1-y} . y\alpha\text{-}Fe_2O_3} \qquad (11)$$

* pw, parts by weight.

The pigment is characterized by an intense hue and high thermal stability and it can be used in all types of ceramic glazes.

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