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Synthesis of Blue–Violet and Brown–Green Zirconium Silicate Pigments from Zircon Mineral

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ABSTRACT

Zirconium silicate (zircon) pigments of blue–violet and brown–green colour have been prepared from zircon mineral as the starting raw material. In the first step this material was decomposed with a waste mixture of NaOH–KOH. In the second step the pigments were synthesized with application of chromium (III) oxide and cobalt (II) dihydrogenphosphate as the chromophores. The optimum conditions for the syntheses of both pigments have been estimated, the properties of the products determined, the reasons for their colour explained and their applicability to ceramic glazes evaluated.

INTRODUCTION

We have previously described a process for the relatively feasible production of some zircon pigments from the cheap starting raw material, zircon mineral (viz. a general procedure,[1] preparation of blue–green[2] and of pink–violet pigments[3]). In the first step the zircon mineral is decomposed by alkali fusion with a mixture of NaOH and KOH (mol. ratio 1:1) available as a waste material from the machine industry. In an intermediate stage of modification of the decomposition products the halide component only is added (as a way of wetting the product with a mixture of HF and HCl), followed by the chromophore. In the second step, the modified decomposition products are calcinated to give the pigments. In our previous papers we used V_2O_5 for a blue–green pigment[2] and $FeCl_2 . 4H_2O$ for a pink–violet pigment as the chromophores.

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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 mineral, giving pigments of desired quality and in good yields. We therefore tried to apply some other chromophores to the reaction mixture, namely those known from the preparation of zircon pigments in the classical one-step process (i.e. from ZrO_2 as the zircon (IV) starting raw mineral). These chromophores included chromium (III) oxide[4] and cobalt (II) dihydrogenphosphate.[5] It was thus possible to synthesize zircon pigments of blue–violet[6] and brown–green[7] colour, as described in this present communication.

EXPERIMENTAL

The starting material was a zircon mineral of Australian origin (content 96% $ZrSiO_4$; finely ground, with prevailing grain size 1–4 μm).[8] The basic mixture for preparation of the pigments was formed from 10 parts of this zircon decomposed with 4 parts of the NaOH and KOH mixture at 750–800°C for a period of 1·5–2 h; after cooling, 8·6 parts of 20% HF and 8·4 parts of 15% HCl were added.[1,2] The pigments were synthesized after the addition of the chromophores. In the case of the blue–violet pigment we used cobalt (II) dihydrogenphosphate as the chromophore, and in the case of the brown–green pigment the chromophore was chromium (III) oxide. On the basis of preliminary experiments, the chromophores were applied in amounts corresponding to 3·5 parts of $Co(H_2PO_4)_2 . 2H_2O$ and 1·5 parts Cr_2O_3.

The most suitable conditions (temperatures and calcination times) for production of the pigments by calcination of the mixture were determined, and variations of the chromophore content were also used, thereby changing the hue of the pigments. The pigments obtained were applied to two types of ceramic glazes—a medium-temperature one (glazing temperature 1050°C) and a high-temperature one (1300°C).

After the calcinations the calcinates were always extracted with 15% HCl (10 min boiling). They were evaluated from the standpoint of the degree of conversion to the pigment (by the method developed in our laboratory[9]) and of the colour. The colour intensity was measured with both the powdered pigments and with glazes containing 10% w/w of the pigments, as the reflectance in the visible region using a Specol 10 apparatus with a remission adaptor R 45/0 (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.

RESULTS AND DISCUSSION

In the temperature interval from 550 to 1000°C (the calcination time was always 1 h) the mixtures were calcinated; the content of chromophores was 3·5 parts of $Co(H_2PO_4)_2 . 2H_2O$ or 1·5 parts of Cr_2O_3, denoted as Co-IV and Cr-IV, respectively, in the table. Figure 1 presents the degree of conversion of the calcinates into the pigments at various temperatures. It can be seen that for the blue–violet pigment a sufficient degree of conversion is attained above 750°C and a steady-state (maximum) degree of conversion above 850°C. For the brown–green pigment the steady-state degree of conversion is attained as low as 800°C; the overall degree of conversion of the calcinate into the brown–green pigment is more than 10% lower (about 75%) than in the case of the blue–violet pigment. From Figs 2 and 3 it can be seen that the pigments and the glazes made therewith have pink–violet and brown–green colour, the most suitable temperatures for their production being 850 and 800°C, respectively.

The chemistry of formation of zirconium (IV) silicate as the basis of both pigments can be described by eqns (1)–(6). The starting decomposition products are *de facto* alkali silicozirconates (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 (3).

$$M_2ZrSiO_5 + 2HX = (H_2ZrSiO_5) + 2MX \quad (1)$$

$$H_2ZrSiO_5 + H_2O = H_2ZrO_3 + H_2SiO_3 \quad (2)$$

$$H_2ZrO_3 + H_2SiO_3 = ZrO_2 + SiO_2 + 2H_2O \quad (3)$$

At higher calcination temperatures the mineralizer of the alkali halide 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 by 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, these halogens are shielding the large mutual repulsive forces of zirconium (IV) and silicon (IV) ions, thus enabling

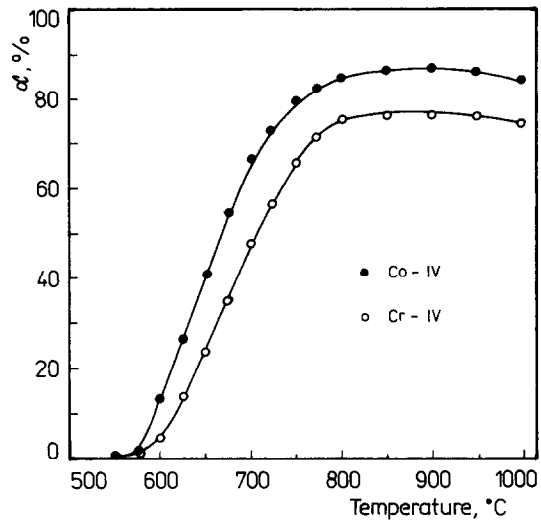


Fig. 1. The dependence of the degree of conversion (α) of the mixtures Co-IV and Cr-IV (see Table 1) to blue–violet and brown–green pigments on the calcination temperature (for calcination time 1 h).

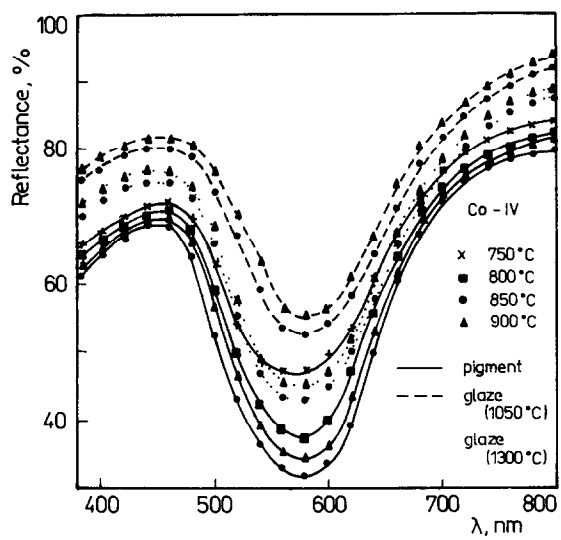


Fig. 2. The colour of the blue–violet pigments (——), synthesized using the mixture Co-IV (see Table 1) and at temperatures of 750°C (×), 800°C (■), 850°C (●) and 900°C (▲) (for time 1 h); and the colour hue of middle-temperature glaze (temperature of glazing 1050°C; – – –) and high-temperature glaze (1300°C, ····) with 10% (w/w) pigments.

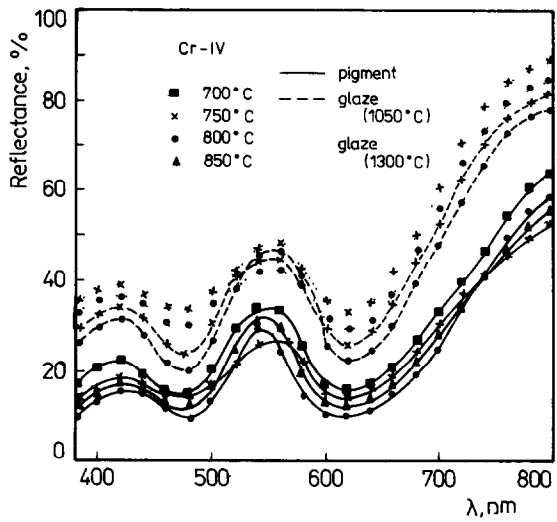


Fig. 3. The colour of the brown–green pigments (——) synthesized using the mixture Cr-IV (see Table 1) at temperatures 700°C (■), 750°C (×), 800°C (●) and 850°C (▲) (for time 1 h); the colour hue of middle-temperature glaze (temperature of glazing 1050°C; – – –) and high-temperature glaze (1300°C, ····) with 10% (w/w) pigments.

their mutual approach and reaction.[11–13] Similar favourable effects are also observed with oxygen, which is intermediate between fluorine and chlorine in its electronegativity.[13,14] Therefore, every change in its amount in the calcinated mixture (e.g. due to the reaction of chromophore) also became apparent in the conditions of the pigment synthesis.[15] In this respect the chromophore $Co(H_2PO_4)_2 . 2H_2O$ used for the blue–violet pigment is practically inert. Therefore the temperature dependence of the conversion of the calcinate into the blue–violet pigment is comparable with a similar dependence for the synthesis of pure (non-coloured) zirconium (IV) silicate[1] without any chromophore. The reason is that cobalt (II) dihydrogenphosphate undergoes only dehydration (and condensation) reactions during calcination; it gradually releases two molecules of water of crystallization (beginning at 150 and 180°C; eqn (7)[11]) and two further molecules of water (beginning at 250 and 350°C, respectively)[11] to give the first condensation products $CoH_2P_2O_7$ [eqn (8)] and then the second product $Co_2P_4O_{12}$ [eqn (9)].

$$Co(H_2PO_4)_2 . 2H_2O = Co(H_2PO_4)_2 + 2H_2O \quad (7)$$

$$Co(H_2PO_4)_2 = CoH_2P_2O_7 + H_2O \quad (8)$$

$$CoH_2P_2O_7 = \tfrac{1}{2}Co_2P_4O_{12} + H_2O \quad (9)$$

The formation of the colouring particles of cyclotetraphosphate is complete at temperatures of about 600°C. These are temperatures at which the first

$ZrSiO_4$ microcrystals are formed in the calcinated mixture. The colouring particles of $Co_2P_4O_{12}$ just formed are effectively incorporated into these microcrystals, thus producing the blue–violet hue [eqns (10) and (11)].

$$(1-x)(M_2SiO_3) + (1-x)ZrO_2 + xCo_2P_4O_{12} = (ZrSiO_4)_{1-x}.xCo_2P_4O_{12} + (1-x)M_2O \quad (10)$$

$$(1-x)ZrO_2 + (1-x)SiX_4 + (1-x)O_2 + xCo_2P_4O_{12} = (ZrSiO_4)_{1-x}.Co_2P_4O_{12} + 2(1-x)X_2 \quad (11)$$

When applying this pigment to the high-temperature glaze we found that the intensity of the blue–violet pigment continued to increase (Fig. 2), which agrees with the fact that at temperatures above 1060°C the inclusions begin to melt and are transformed into vitreous higher linear phosphates[16] [eqn (12)].

$$nCo_2P_4O_{12} = 2[Co(PO_3)_2]_n \quad (12)$$

These products, then, are more intensely coloured than the cyclotetraphosphate,[17] and the general formula of the pigment reads as follows:

$$(ZrSiO_4)_{1-x}.\frac{2x}{n}Co(PO_3)_{2n}$$

In the sense described above the chromophore Cr_2O_3 for the synthesis of the brown–green pigment can be considered only partially inert. When the $ZrSiO_4$ microcrystals are formed [eqns (5) and (6)], a part of the Cr_2O_3 is only mechanically incorporated into them [eqns (13) and (14)], the chromium oxide itself remaining chemically practically unchanged. It then represents the source of the green coloration of the pigment.

$$(1-x)(M_2SiO_3) + (1-x)ZrO_2 + xCr_2O_3 = (ZrSiO_4)_{1-x}.xCr_2O_3 + (1-x)M_2O \quad (13)$$

$$(1-x)ZrO_2 + (1-x)SiX_4 + (1-x)O_2 + xCr_2O_3 = (ZrSiO_4)_{1-x}.xCr_2O_3 + 2(1-x)X_2 \quad (14)$$

For the formation of the brown component of the colour of the pigment, the following hypothesis is suggested. The relatively large number of alkali ions present in the melt phase in the reaction mixture obviously enables a very small part of chromium ions to be tranformed to a higher-valence state (Cr^{VI}). This occurs during the formation of $ZrSiO_4$; hence these ions can enter its tetragonal structure by substitution as positively charged defects (obviously predominantly replacing zirconium–$Cr_{Zr}^{\cdot\cdot}$). They represent the source of the brown coloration of the pigment; their extra positive charge is

compensated by incorporation of a small amount of alkali ions, again replacing the zirconium, as negatively charged defects M'''_{Zr} [eqn (15)].

$$(M_2SiO_3) + (1-y)ZrO_2 + 0{\cdot}3yCr_2O_3 + 0{\cdot}45yO_2 = Zr_{1-y}M^{I}_{0{\cdot}4y}Cr^{IV}_{0{\cdot}6y}SiO_4 + (1-0{\cdot}2y)M_2O \quad (15)$$

It can be seen from eqn (15) that the oxidation of a smaller part of the chromophore (Cr^{III} to a higher valence) consumes a small amount of oxygen from the reaction mixture, which weakens the mineralization action of the oxygen present in the mixture and obviously causes an overall decrease in the degree of conversion of the calcinate into the pigment (as compared with the synthesis of both the blue–violet pigment and pure $ZrSiO_4$).[1] Reactions (13)–(15) proceed simultaneously; hence they result in the brown–green hue of the final pigment, its general formula being:

$$(Zr_{1-y}M^{I}_{0{\cdot}4y}Fe^{VI}_{0{\cdot}6y} \cdot SiO_4)_{1-x} \cdot xCr_2O_3$$

In order to confirm the above reasoning for the basis of the colour of both the pigments, they were submitted to X-ray diffraction and electron microscopy. For this purpose the calcinates were intensively extracted to remove the parts of colouring particles ($Co_2P_4O_{12}$, Cr_2O_3) which were not incorporated into some silicate crystals as inclusions but remained as a second phase in the product. Due to their difficult solubility, the calcinates had to be extracted at first by prolonged (several days) boiling with a mixture of HF and H_2SO_4,[9] followed by a similarly prolonged boiling with 10% NaOH solution. These extractions removed free particles of $Co_2P_4O_{12}$ and/or Cr_2O_3 without affecting the pigment microcrystals, which were well developed. This was confirmed by electron microscopy. (The colour intensity of the pigments was thereby not much changed, which confirms the presumption that a greater part of the colouring particles of $Co_2P_4O_{12}$ or Cr_2O_3 is incorporated into the microcrystals and thus protected by a thin layer of $ZrSiO_4$.) The magnitude of the microcrystals of both pigments was almost regular, about 5 μm. The 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: $a_0 = 0{\cdot}660\,22$ nm, $c_0 = 0{\cdot}598\,03$ nm for the blue–violet pigment and $a_0 = 0{\cdot}660\,15$ nm, $c_0 = 0{\cdot}597\,90$ nm for the brown–green pigment. Hence in the first case the structural parameters are practically identical with those of the pure zirconium (IV) silicate obtained in the same way (without any chromophore); in the second case they are slightly lower. The identity of the parameters of the blue–violet pigment with those of pure $ZrSiO_4$ confirms, to some extent, the fact that no ions with radii distinctly different from Zr^{IV} are incorporated markedly into the pigment structure. The lower values of the structural parameters of the brown–green pigment, on the other hand,

indicate an incorporation of a limited number of chromium ions with higher valence (and smaller ionic radius) into the $ZrSiO_4$ structure; these ions replace the zirconium ions (of greater ionic radius) as positively charged substitution defects. Although their incorporation is compensated by the incorporation of larger ions of alkali metals (predominantly Na), the result is the lowering of the structural parameters. With regard to the condition of electroneutrality, only one half of the sodium ions enter the $ZrSiO_4$ structure compared with chromium [eqn (15)] and, in addition, the sodium ions are larger than the Zr ions which are replaced, but the difference is less than that between Zr ions and the smaller Cr ions of higher valence.

Both the pigments exhibit very weak but perceptible diffraction lines which could be assigned to $Co_2P_4O_{12}$ (in the blue–violet pigment) and Cr_2O_3 (in the brown–green pigment). After bisque firing of the blue–violet pigment at 1100°C these diffraction lines disappeared, which confirms the transition of inclusions of crystalline type ($Co_2P_4O_{12}$) into vitreous inclusions ($/Co(PO_3)_2/n$) [eqn (12)]. As the pigments were thoroughly extracted in advance, the above-mentioned results confirm the fact that in both the pigments these colouring particles can only exist as inclusions within the pigment microcrystals. (In the case of the brown–green pigment the basic $ZrSiO_4$ pigment structure also contains chromium ions of higher valence.) These results agree with the above-suggested principles of the colour origin of pigments (see the general equations).

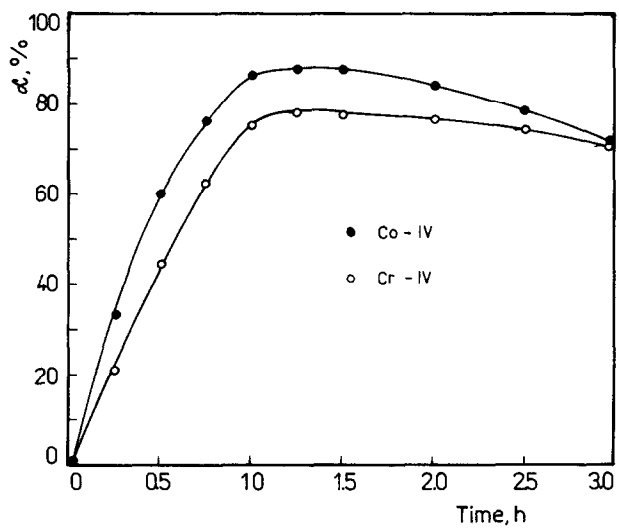


Fig. 4. The dependence of the degree of conversion (α) of the mixtures Co-IV and Cr-IV (see Table 1) to blue–violet and brown–green pigments on the calcination time for a calcination temperature of 850°C for Co-IV and 800°C for Cr-IV.

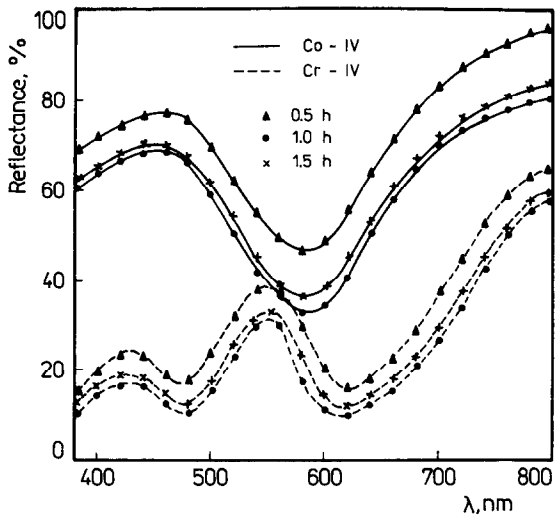


Fig. 5. The colour of the blue–violet pigments (——) and brown–green pigments (– – –) synthesized using the mixture Co-IV and Cr-IV (see Table 1) and at the calcination times of 0·5 h (▲), 1 h (●) and 1·5 h (×) at temperatures of 850°C (Co-IV) and 800°C (Cr-IV).

At the temperatures chosen, i.e. 850°C for the blue–violet pigment and 800°C for brown–green pigment, the degree of conversion of the calcinate into the pigment as a function of the calcination time was assessed (Fig. 4). It was found that maximum conversion was achieved after 60–90 min calcination, and further prolongation (especially above 120 min) resulted in a decrease of degree of conversion. The reason lies in the much too high alkali content in the mixture calcinated; after the mildly exothermic reaction of the pigment synthesis is complete, the alkalis obviously decompose the product formed, because they are acting similarly as in an alkaline fusion. Also the colour intensity of the pigments prepared at 850 and 800°C, respectively, at various times of calcination and that of the glazes coloured therewith show that the calcination time of 60–90 min represents the optimum at the temperatures mentioned (Fig. 5).

Furthermore, the influence of the content of chromophore [$Co(H_2PO_4)_2 . 2H_2O$ or Cr_2O_3] in the mixture on the colour of the pigment was evaluated. The proportion of chromophores in the decomposition products which were prepared by alkali melting of zircon with the waste mixture of NaOH–KOH and sprayed by HF and HCl (i.e. using the same method as in the case of the mixtures above with a content of 3·5 parts $Co(H_2PO_4)_2 . 2H_2O$ or 1·5 parts Cr_2O_3) was changed within the range 0·75–4·5 or 0·6–1·8 parts (see Table 1).

The pigments were synthesized at temperatures of 850°C (blue–violet) or 800°C (brown–green) for 60 min. The colour of the pigments, expressed by

TABLE 1
Contents of $Co(H_2PO_4)_2 . 2H_2O$ and Cr_2O_3 in the Mixtures for the Preparation of Blue–Violet and Brown–Green Pigments

Mixture No.	*$Co(H_2PO_4)_2 . 2H_2O$ content (parts)*	*Mixture no.*	*Cr_2O_3 content (parts)*
Co-I	0·75	Cr-I	0·6
Co-II	1·5	Cr-II	0·9
Co-III	2·5	Cr-III	1·2
Co-IV	3·5	Cr-IV	1·5
Co-V	4·5	Cr-V	1·8

the reflectance in the visible range of the spectrum, are shown in Figs 6 and 7. For the required blue–violet and brown–green hues, the mixtures Co-IV and Cr-IV (i.e. with 3·5 parts of $Co(H_2PO_4)_2 . 2H_2O$ or with 1·5 parts Cr_2O_3 corresponding to approximately 20 wt% and 10 wt% chromophore in the dry mixture) proved to be the most suitable. The colour of the middle-temperature and/or high-temperature glazes with 10% pigments (see Figs 8 and 9) confirmed the very good thermal stability of the pigments. The dye glazes were of the corresponding blue–violet or brown–green colour. In addition, it also proved useful to submit the blue–violet pigment to bisque firing at 1060–1100°C [see the colour intensity of the high-temperature glaze (Fig. 8)].

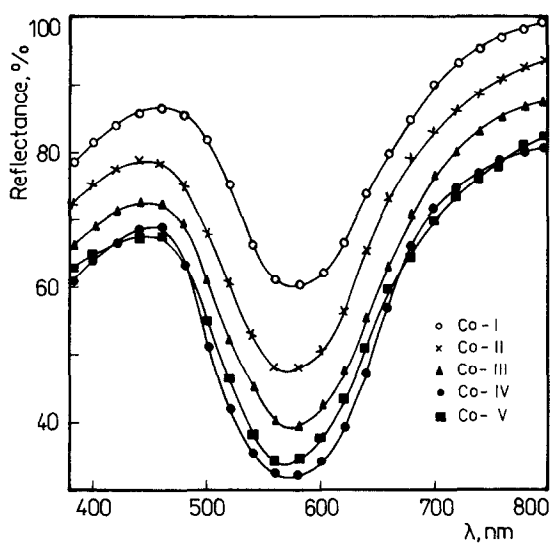


Fig. 6. Effect of the content of chromophore $Co(H_2PO_4)_2 . 2H_2O$ in the mixtures Co-I–V (see Table 1) on the colour of the blue–violet pigment (calcination temperature 850°C for 1 h).

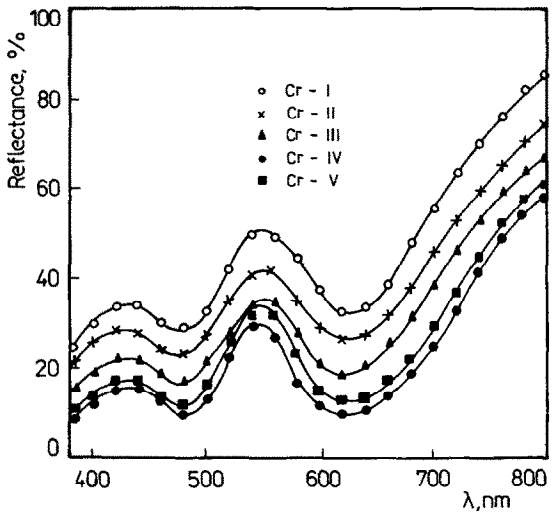


Fig. 7. Effect of the content of the chromophore Cr_2O_3 in the mixtures Cr-I–V (see Table 1) on the colour of the brown–green pigment (calcination temperature 800°C for 1 h).

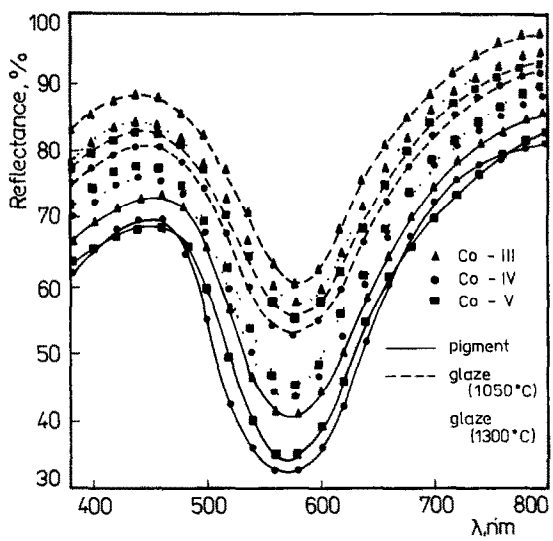


Fig. 8. Effect of the content of the chromophore $Co(H_2PO_4)_2 . 2H_2O$ in the mixtures Co-III, Co-IV and Co-V (see Table 1) on the colour of the blue–violet pigment (calcination temperature 850°C for 1 h) and the colour of middle-temperature glaze (temperature of glazing 1050°C; – – –) and high-temperature glaze (1300°C; ····) with 10% (w/w) pigments.

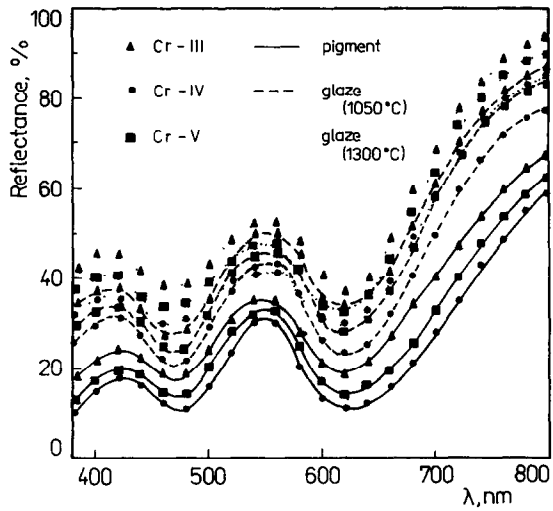
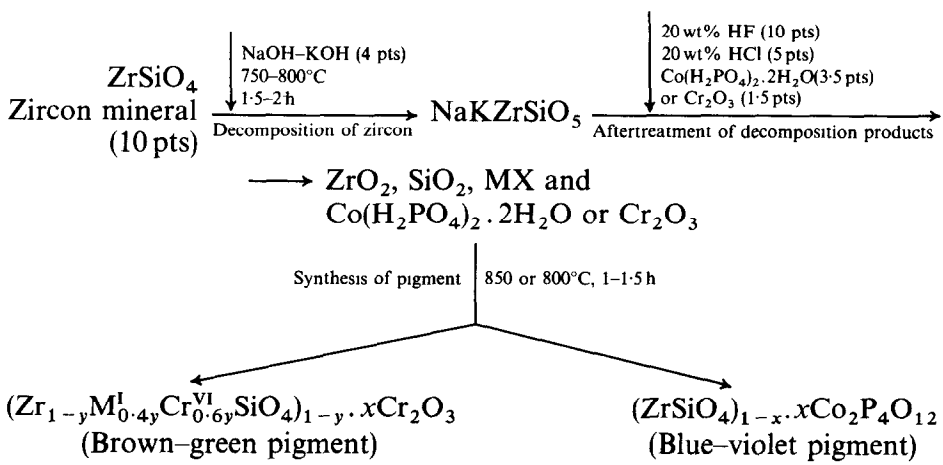


Fig. 9. Effect of the content of the chromophore Cr_2O_3 in the mixtures Cr-III, Cr-IV and Cr-V (see Table 1) on the colour of the brown–green pigment (calcination temperature 800°C for 1 h) and the colour of middle-temperature glaze (temperature of glazing 1050°C; – – –) and high-temperature glaze (1300°C; ····) with 10% (w/w) pigments.

CONCLUSION

According to the process[6,7] proposed in this work, the synthesis of blue–violet and brown–green zirconium silicate pigments of mineral zircon can be described by Scheme 1.



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

Scheme 1

The pigments are characterized by an intense colour and high thermal stability, and can be applied to all kinds of ceramic glazes.

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