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# A Blue-Violet Zirconium Silicate Pigment with Admixtures of Condensed Cobalt Phosphates

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## SUMMARY

*The zirconium silicate described represents a pigment of a new hue and is suitable for ceramics. Its colour is due to particles of condensed cobalt phosphates incorporated as the so-called inclusions in zirconium silicate microcrystals. A combination of disodium hexafluorosilicate and lithium hydroxide with cryolite has been used as the mineralizer in the pigment synthesis. The chromophore is cobalt dihydrogen phosphate or the corresponding mixture of cobalt(II) oxide and phosphoric acid, which are calcined to give intensely coloured particles of the condensed cobalt phosphate. The effects of the chromophore and of the individual components of the mineralizer on the colour hue of the pigment have been evaluated and their optimum amount in the starting mixture estimated. The calcination temperatures found and the yields of products correspond to other zirconium silicate pigments. The consumption of expensive cobalt is very low, and the pigment is applicable to all kinds of ceramic glazes.*

## 1 INTRODUCTION

The zirconium silicate pigments represent a modern type of ceramic pigment of high quality. They exhibit high thermal, chemical and colour stability and can be used for colouring a variety of ceramic glazes. The pigments are based on the zirconium silicate formed during their synthesis and possess the structure of zircon mineral.[1] They are usually prepared by calcination of mixtures of the basic starting oxides ($ZrO_2$ and $SiO_2$), together with mineralizers and the so-called chromophores. Although the pure silicate is colourless, it can become coloured during the synthesis in two ways.[2] One way consists in trapping of some ions in the silicate structure in the form of colouring defects.[1,3–6] The best known representatives of this group are the blue pigment[3,7] $Zr_{1-x}V_xSiO_4$ and the yellow pigment[4] $Zr_{1-x}Pr_xSiO_4$. The colour of these is due to uncharged substitution defects of tetravalent vanadium ions or praseodymium ions instead of zirconium[3–7] ($V^{x}_{Zr}$ or $Pr^{x}_{Zr}$). The second group of zirconium silicate pigments is represented by the pigments coloured by so-called inclusion.[2,3–6] The inclusions are intensely coloured particles of some compounds which are incorporated into the zircon microcrystals during their formation. The protective layer of zirconium silicate covering these particles then serves in the subsequent application as a protection against aggressive glaze melt. The particles alone would not be resistant to this medium and would not retain their colouring ability. Known pigments of this type include, for example, the pink[2,5,8] $ZrSiO_4.x\alpha\text{-}Fe_2O_3$ and the orange[2,6] $ZrSiO_4.xCd(S,Se)$ pigment.

There also exists a blue-grey[9] zirconium silicate pigment whose preparation is based on the addition of cobalt(II) halide or sulphate to the starting mixture. This pigment represents a combination of the above two ways of coloration. Part of the cobalt, in the form of trivalent ions, is trapped in the zirconium silicate structure as negatively charged lattice defects $Co'_{Zr}$ and causes the grey hue. The other part, in the form of particles of cobalt(II) oxide or silicate, is present in the pigment prepared either individually or as inclusions incorporated in the zircon microcrystals. These particles or inclusions impart a blue hue to the product, so that the resulting hue is blue-grey. However, when used in the direct coloration of ceramic glazes, and especially in glazes which need high temperatures of about 1300°C for glazing, this pigment causes a mechanical unevenness of the glaze surface. This can be partially remedied by the action of hot mineral acids on the pigment before its application, the process involving the extraction of the free particles of cobalt compounds. However, this extraction is a delicate operation, and moreover, the preparation of the pigment consumes relatively large amounts of cobalt. This present communication describes the preparation of a cobalt-containing zirconium silicate pigment which does not have the above drawbacks. The new product is a blue-violet zirconium silicate pigment containing condensed phosphates of cobalt[10] and for which the following schematic formula is used in the text: $ZrSiO_4.x[Co(PO_3)_2]_n$.

## 2 EXPERIMENTAL

The starting oxides used in the preparation of the mixtures for the synthesis of the pigment were $ZrO_2$-7 (Goldschmidt) of 97·7% (w/w)[7] purity and

$SiO_2$ from Austria.[7] These oxides of natural origin are used industrially for the syntheses of pigments of the zirconium silicate type.

When formulating the starting mixtures we adopted the earlier suggested mineralizer which had proved useful in the synthesis of the pink zirconium silicate pigment of the inclusion type,[11] i.e. $ZrSiO_4 . x\alpha\text{-}Fe_2O_3$. This mineralizer contains $Na_2SiF_6$, LiOH and molybdenum(VI) oxide or its ammonium or alkali salts. After preliminary experiments, the molybdenum compound was replaced by cryolite, which proved more suitable for the synthesis of the $ZrSiO_4 . x[Co(PO_3)_2]_n$ pigment. Comparison was also made on the effect of the amount of the mineralizer in the starting mixtures and on the effect of the mutual ratio of its individual components on the pigment quality (hue). For the chromophore, cobalt(II) dihydrogen phosphate was used; this is gradually transformed by calcination into cobalt(II) cyclotetraphosphate,[12] which exhibits a high colour, and very good chemical and thermal stability. The effect of the amount of chromophore on the pigment quality was also studied. It was found that a mixture of cobalt(II) oxide, carbonate or hydroxide with phosphoric acid also produced the tetraphosphate on calcination and could thus be used as a cheaper chromophore.

The starting mixtures containing the basic oxides, mineralizer and chromophore were homogenized in an agate mortar. The temperature region of formation of the pigment was followed by thermal analysis[13] using a Derivatograph Q-1500 apparatus (MOM, Budapest). The mixtures were then calcined at the selected temperature in porcelain crucibles in an electric resistance furnace. The calcinates were extracted with hot hydrochloric acid (1:1) to remove soluble residues of the mineralizer. The extracted calcinates were submitted to gravimetric analysis[14] to determine the content of pure zirconium silicate pigment.

The colour hue of the pigment was evaluated by measurements of spectral reflectance in the visible region using a Spekol 10 apparatus with the R45/0 reflectance adapter (Zeiss, Jena). The pigments prepared were applied to ceramic glazes at medium and high temperatures, i.e. at glazing temperatures of 1000 and 1300°C, respectively. The final glazes were evaluated with regard to their colour hues and the mechanical evenness of their surfaces.

## 3 RESULTS AND DISCUSSION

Thermal analysis (TA) provided information about the temperature regions of formation of the pigment investigated and also about the effect of the mineralizer and chromophore components on the pigment synthesis

(Fig. 1). The TA was initially applied to a mixture containing the oxides ($ZrO_2$ and $SiO_2$), together with two mineralizer components, viz. $Na_2SiF_6$ and $LiOH.H_2O$ (curves S), cryolite, $Na_3AlF_6$, was then added (curves P), and finally TA was applied to the complete starting mixture for the synthesis of the pigment, i.e. with addition of the chromophore $Co(H_2PO_4)_2.2H_2O$ (curves $P_5$). The temperature increased at a rate of 10°C per min during the TA, which corresponds to the temperature increase in the electric resistance oven used for the subsequent calcinations.

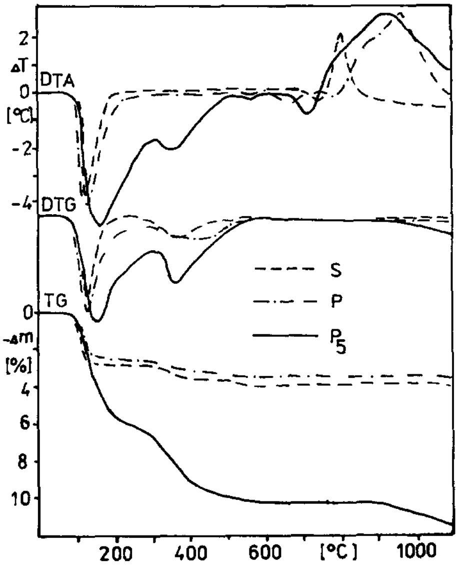

**Fig. 1.** Thermal analyses of the S, P and $P_5$ mixtures. Mixtures (mg): S, 800 $ZrO_2$ + 360 $SiO_2$ + 80 $Na_2SiF_6$ + 80 $LiOH.H_2O$; P, S + 240 $Na_3AlF_6$; $P_5$, P + 400 $Co(H_2PO_4)_2.2H_2O$. Temperature increase 10°C/min; sensitivity, TG 200 mg, DTA and DTG 1/5; standard, $\alpha$-$Al_2O_3$; atmosphere, air; crucible, Pt with a lid.

The TG curves show, above 100°C, a mass decrease corresponding to the release of a molecule of crystal water from lithium hydroxide [eqn (1)]. In the case of $P_5$ this decrease is immediately followed by the release of crystal water from the chromophore [eqn (2)]:

$$LiOH.H_2O = LiOH + H_2O \tag{1}$$

$$Co(H_2PO_4)_2.2H_2O = Co(H_2PO_4)_2 + 2H_2O \tag{2}$$

The chromophore then gradually releases two molecules of constitutional water, commencing at 250 and 350°C respectively,[12] to give the first condensation products $CoH_2P_2O_7$ [eqn (3)] and then the second product cyclo-$Co_2P_4O_{12}$ [eqn (4)]:

$$Co(H_2PO_4)_2 = CoH_2P_2O_7 + H_2O \quad (3)$$

$$CoH_2P_2O_7 = \tfrac{1}{2}\text{cyclo-}Co_2P_4O_{12} + H_2O \quad (4)$$

The formation of colouring particles of cyclotetraphosphate is, under the conditions of TA, complete at temperatures of about 600°C. This process is also connected with the release of $\frac{1}{2}H_2O$ from LiOH due to the slow reaction with $SiO_2$, giving a compound of the lithium silicate type [eqn (5)] and with the reactions with $Na_2SiF_6$ [eqn (9)] and $Na_3AlF_6$ [eqn (12)]. The formation of zirconium silicate (see below) itself commences at temperatures of 720–730°C in the S mixture, the relatively sharp maximum of this exothermic process being at 790°C. When using cryolite in the starting mixture P, this reaction occurs at higher temperatures, its beginning and maximum being at 750–780°C and 860°C, respectively. The exothermic effect is greater and extends over a broader temperature region. Interestingly, the addition of the chromophore (curve $P_5$) resulted in a great exothermic effect on the DTA curve overlapping the two original exothermic effects (S, P). Hence the chromophore must also contribute to the pigment formation proper. This can be due to the smaller part of it being converted to alkali phosphate by a reaction with the alkali components of the mineralizer during the calcination. The alkali phosphate then effectively combines the mineralization action of $Na_2SiF_6$, LiOH and cryolite into a practically single continuous and slow process. The slower course of synthesis then allows a more efficient incorporation of colouring particles of cyclo-$Co_2P_4O_{12}$ into microcrystals of the zirconium silicate formed.

On the basis of the TA results we selected a temperature of 850°C and a time of 1·5 h for the subsequent calcination experiments; these conditions were sufficient for the pigment synthesis. The pigment calcinates were prepared from the starting mixtures in which variations were made in the two basic components of the mineralizer (i.e. $Na_2SiF_6$ and $LiOH.H_2O$) (Table 1, mixtures M), the cryolite content (Table 1, mixtures K) and finally the $Co(H_2PO_4)_2.2H_2O$ content (Table 1, mixtures P).

The calcinates were extracted with hot hydrochloric acid and evaluated with regard to their colour hue (Fig. 2).

The presence of lithium hydroxide in the mixture was found to be necessary; in its absence the calcinates were very pale or even white. This ingredient decreases the temperature of formation of zirconium silicate[13] and thus shifts it towards the temperatures of formation of coloured inclusions of dicobalt(II) cyclotetraphosphate. The hydroxide reacts with the grains of starting silicon oxide [eqn (5)] and thus forces them to react in

TABLE 1
Composition of the Basic Mixtures for Evaluation of the Mineralizer Components (M), the Cryolite Content (K) and the Chromophore Content (P)

| *Mixtures* | *Basic composition (g)* | | | | | |
|---|---|---|---|---|---|---|
| | *$ZrO_2$* | *$SiO_2$* | *$Na_2SiF_6$* | *$LiOH.H_2O$* | *$Na_3AlF_6$* | *$Co(H_2PO_4)_2.2H_2O$* |
| M[a] | 20 | 9 | — | — | 6 | 10 |
| K[b] | 20 | 9 | 2 | 2 | — | 10 |
| P[c] | 20 | 9 | 2 | 2 | 6 | — |

[a] Mixtures derived from the basic M mixture with varying mineralizer composition: $M_1 = M + 2g\ Na_2SiF_6$; $M_2 = M + 2g\ LiOH.H_2O$; $M_3 = M + 2g\ Na_2SiF_6 + 2g\ LiOH.H_2O$.

[b] Mixtures derived from the basic K mixture by varying the cryolite content: $K_1 = K + 2g$; $K_2 = K + 4g$; $K_3 = K + 6g$; $K_4 = K + 10g\ Na_3AlF_6$.

[c] Mixtures derived from the basic P mixture by addition of $Co(H_2PO_4)_2.2H_2O$: $P_1 = P + 2g$; $P_2 = P + 4g$; $P_3 = P + 6g$; $P_4 = P + 8g$; $P_5 = P + 10g$; $P_6 = P + 15g$; $P_7 = P + 20g$; $P_8 = P + 25g\ Co(H_2PO_4)_2.2H_2O$.

the synthesis of zirconium silicate [eqn (10)]; moreover, it partially decomposes the other components of the mineralizer into reactive intermediates [eqns (6) and (12)]. The presence of disodium hexafluorosilicate is important for initiating the reaction of formation of the silicate. By the action of the calcination temperature and with cooperation of the water vapour released by some reactions, the hexafluorosilicate is, to a smaller extent, also decomposed to sodium fluoride and silicon tetrafluoride [eqn (7)]. The gaseous $SiF_4$ represents a mobile and highly reactive component of the mixture, and it initiates the mildly exothermic reactions involved in the synthesis of the silicate portions of the pigment

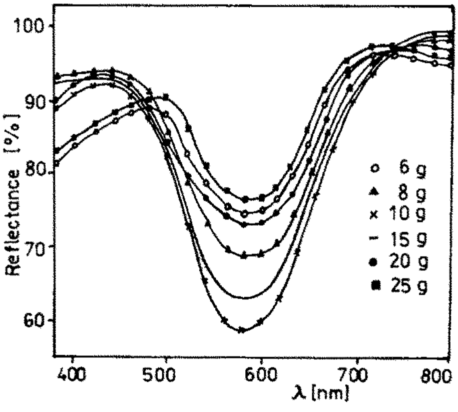

**Fig. 2.** Effect of the amount of $Co(H_2PO_4)_2.2H_2O$ in the $P_{1-8}$ mixtures on the colour hue of the pigment. Calcination temperature, 850°C; time, 1·5 h.

[eqn (8)]. These reactions also involve the alkali silicates [eqns (10) and (11)], which are formed by reactions shown in eqns (5), (6) and (9):

$$2LiOH + SiO_2 = (Li_2SiO_3) + H_2O \tag{5}$$

$$6LiOH + Na_2SiF_6 = (M_2SiO_3) + 6MF + 3H_2O \quad (M = Li, Na) \tag{6}$$

$$Na_2SiF_6 = 2NaF + SiF_4 \tag{7}$$

$$SiF_4 + ZrO_2 + O_2 = ZrSiO_4 + 2F_2 \tag{8}$$

$$4MF + 3SiO_2 = 2(M_2SiO_3) + SiF_4 \tag{9}$$

$$M_2SiO_3 + ZrO_2 + F_2 = ZrSiO_4 + 2MF + \tfrac{1}{2}O_2 \quad (M = Li, Na) \tag{10}$$

$$M_2SiO_3 + ZrO_2 = ZrSiO_4 + (M_2O) \quad (M = Li, Na) \tag{11}$$

The melting temperatures of these silicates, if homogeneous and pure, lie above the temperatures of formation of the pigment. Despite that, they are transferred, in the calcined reaction mixture, into the melt layers at the surface of the grains of the basic oxides.[15] Thus they become mobile components in the mixture and contribute to the transport between the reacting components. However, at the temperatures of the synthesis of the blue-violet zirconium silicate pigment, the decisive part of transport of the silicon component is realized in the form of the reactive gaseous $SiF_4$ which is formed in the mixture by decomposition of disodium hexafluorosilicate and by other reactions (9). In the reaction involving the formation of zirconium silicate (8), the fluorine released from the tetrahalide is extremely important for the synthesis of zircon pigments. Due to their high electronegativity, the fluorine atoms shield the strong repulsive forces[16,17] of silicon(IV) and zirconium(IV) ions, whereby their mutual approach and the reaction proper [eqn (8)] are made possible.

The reactions involved in the pigment synthesis also involve the cryolite, which is known for its mineralization effects, e.g. in the production of garnet pigments. During calcination, cryolite releases, by reaction with lithium hydroxide, lithium and sodium fluorides, together with alkali aluminate [eqn (12)]:

$$Na_3AlF_6 + 4LiOH = MAlO_2 + 6MF + 2H_2O \quad (M = Na, Li) \tag{12}$$

The fluorides then react again with silicon(IV) oxide grains (9), and the aluminate favourably supports the melt component of the reaction mixture. However, the shape of the peak of the exothermic effect recorded by TA (Fig. 1, S) indicates that cryolite somewhat slows down the pigment synthesis proper. Such a slower synthesis taking place in several parallel or subsequent steps is, nevertheless, advantageous for the formation of a zirconium silicate pigment of the inclusion type. It enables a very efficient incorporation of the colouring cyclo-$Co_2P_4O_{12}$ particles formed into the synthesized zircon microcrystals. The most stable and most intensely coloured product was obtained with a mineralizer of the composition $Na_2SiF_6:LiOH.H_2O:Na_3AlF_6 = 1:1:3$, in total amount of about 20% (w/w) of the mixture. The evaluation of the effect of the chromophore content on the colour of pigment (Fig. 2) shows that the optimum composition is that of the $P_5$ mixture (Table 1). Its chromophore-to-mineralizer ratio is 1:1, and its composition (%, w/w) is 40·8 $ZrO_2$, 18·4 $SiO_2$, 4·1 $Na_2SiF_6$, 4·1 $LiOH.H_2O$, 12·2 $Na_3AlF_6$, 20·4 $Co(H_2PO_4)_2.2H_2O$. Therefore, the $P_5$ mixture ($K_3, M_3$) was used further for the evaluation of the other conditions of synthesis of the pigment, its quality and application properties.

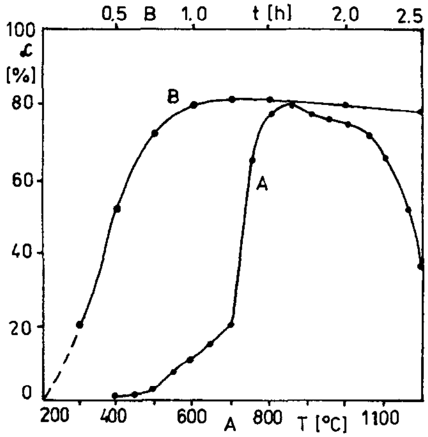

Fig. 3. A, Effect of the calcination temperature of the $P_5$ mixture on its degree of conversion to the pigment. Calcination time, 1·5 h. B, Effect of the calcination time of the $P_5$ mixture on its degree of conversion to the pigment. Calcination temperature, 850°C.

In the calcination temperature region of 400–1200°C and at a calcination time of 1·5 h, the extent of conversion of the extracted calcinates into the pigment was evaluated. From curve A (Fig. 3) it follows that the first portions of zirconium silicate begin to appear in the reaction mixture at temperatures above 550°C, the degree of conversion being sufficient (almost 70%) at temperatures as high as above 750°C. Under these conditions the optimum calcination temperature lies at 850°C, at which temperature the pigment content in the extracted calcinate exceeds 80%. It was found, however, that further increase in the calcination temperature decreases the degree of conversion, this trend being more distinct above 1050°C. This finding can be explained by the relatively high content of the strongly alkaline melt phase in the calcined mixture, which causes, after the completed synthesis of the pigment, its subsequent decomposition [eqns (13) and (14)], especially at enhanced calcination temperatures:

$$(M_2O) + ZrSiO_4 = M_2ZrSiO_5 \qquad (13)$$

$$(M_2O) + M_2ZrSiO_5 = M_2ZrO_3 + M_2SiO_3 \qquad (14)$$

Calcination temperatures of 750–850°C were also found to be optimum from the point of view of the colour hue of the product (Fig. 4). At 850°C, the time dependence of the degree of conversion of the calcinates has also been determined.[14] From Fig. 3, curve B, it is apparent that a period of 1 h is sufficient at this calcination temperature. Above 1·5 h, the degree of conversion is slightly decreased, which is again relatable to the influence of the aggressive alkaline melt on the calcinate, the product being slowly decomposed during prolonged calcination [eqns (13) and (14)].

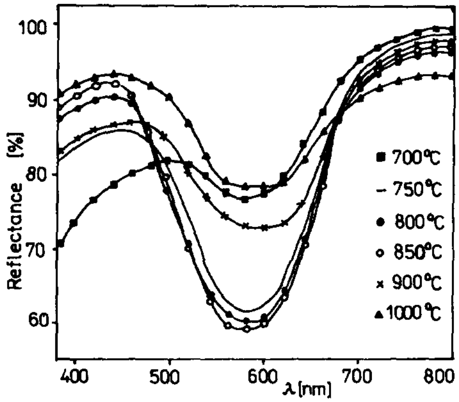

**Fig. 4.** Effect of the calcination temperature (°C) of the $P_5$ mixture on the colour hue of the pigment. Calcination time, 1·5 h.

The pigment prepared under the optimum conditions (the $P_5$ composition of the starting mixture, 850°C, calcination time 1·5 h) was purified by extraction with hot acids (HF and $H_2SO_4$)[14] and analysed. The X-ray diffraction analysis confirmed a pigment structure corresponding to that of the zircon mineral, i.e. the tetragonal space-centred lattice.[1,3-5,8] Also recorded were three intensive diffraction lines corresponding to cyclo-$Co_2P_4O_{12}$,[18] which confirms that the pigment synthesized, but not yet applied to ceramic glazes, contains the colouring particles of cyclo-tetraphosphate. Extraction of the pigment with hot sodium hydroxide solution confirmed that it is incorporated as inclusions in the zirconium silicate microcrystals and is not merely present as the second phase in the calcinate. Such extraction would affect[12] any free particles of cyclo-$Co_2P_4O_{12}$ which would be decomposed and decolourized. The colour hue of the pigment was, however, not changed by the extraction. Electron microscopy also confirmed the compactness of the pigment particles and did not indicate any other type of particles. Their magnitude varied within the limits of 2–5 $\mu$m, which generally corresponds to pigments of the zirconium silicate type.[3-5,8] The shape of the particles is also comparable with that of other pigments, but their surface is less uniform and more folded. This finding is in accordance with the specific surface, which is roughly three to five times greater than of other zirconium silicate pigments.[3-5] This factor is relatable to the more complex mechanism of formation of the pigment studied in this present investigation. The zirconium silicate is formed gradually, and the process is affected by the above-mentioned influence of the aggressive alkaline melt, the amount of which in the mixture is greater than that in the syntheses of other pigments of the same type[3-5,8] and which somewhat attacks the surface of the pigment microcrystals formed.

The prepared pigment was used for the coloration of two basic types of ceramic glazes. In an amount of 7% (w/w) it was applied to a medium-temperature borosilicate glaze and to a high-temperature aluminosilicate at glazing temperatures of 1000 and 1300°C, respectively. In both cases pure blue-violet hues without grey admixtures were obtained, and the colour of glazes corresponded to that of the pigments. The glazes were, after the coloration, glossy, smooth and without any signs of surface unevenness. The coloration was distinctly more intense in the case of the high-temperature glaze; this was already signalized by the pigment synthesis at the temperatures of 1100 and 1200°C. At 1060°C, cyclo-$Co_2P_4O_{12}$ melts and the colouring inclusions are transformed into more intensely coloured glassy products of higher linear cobalt phosphates[19] [eqn (15)]:

$$\frac{n}{2}\text{cyclo-}Co_2P_4O_{12} = [Co(PO_3)_2]_n \qquad (15)$$

These products are quite thermostable and do not revert back to the cyclotetraphosphate on cooling the glaze (or pigment) or by its repeated heating (which would occur if they were in pure form[19]). This occurs since the melt of higher linear phosphates attacks, to a small but definite extent, the zirconium silicate shell from the inside. A small part of the silicate and zirconium components are transferred into the phosphate melt and thereby stabilize its macromolecular chains which, after solidification, represent intensely coloured inclusions of a vitreous amorphous character. Hence it would be useful to anneal the pure pigment at this temperature for a short time, e.g. several minutes prior to its application as medium- or low-temperature glazes, i.e. at glazing temperatures below 1060°C. Before the annealing, however, the pigment must be extracted with water or, preferably, with dilute mineral acid in order to remove the residual alkaline components in the product from the mineralizer. These components would otherwise cause decomposition (see Fig. 3).

Since the final zirconium silicate pigment contains inclusions formed by higher linear cobalt phosphates of approximate formula $[Co(PO_3)_2]_n$, the whole pigment is denoted by the overall schematic formula $ZrSiO_4 . x[Co(PO_3)_2]_n$. Analyses of the alkaline and acid extracts of the pigment showed that roughly 85% (for the $P_5$ mixture) of the condensed cobalt phosphates are effectively (i.e. non-extractably) trapped in the form of inclusions. This result and the degree of conversion found for the pigment allowed the determination of the $x$ value (0·18) by calculation (for the pigment prepared under the optimum conditions: the $P_5$ mixture, calcination temperature 850°C, time 1·5 h).

## 4 CONCLUSION

The blue-violet zirconium silicate pigment is best prepared by the procedure suggested in this communication from the starting mixture ($P_5$) containing (%, w/w): 40·8 $ZrO_2$, 18·4 $SiO_2$, 4·1 $Na_2SiF_6$, 4·1 $LiOH . H_2O$, 12·2 $Na_3AlF_6$, 20·4 $Co(H_2PO_4)_2 . 2H_2O$. Advantageous calcination temperature and time are 800–850°C and 1–1·5 h, respectively. The pigment exhibits high thermal and chemical stability and can be applied to all types of ceramic glazes including those requiring high temperatures, i.e. glazing temperatures of 1300°C. When used in the amount of 3–7% (w/w) it effectively imparts the same blue-violet hue to these glazes. The coloured glazes are smooth, glossy and without any surface unevenness. When applied to glazes with glazing temperatures below 1060°C, the pigment should be extracted with water or dilute mineral acid and then annealed at this temperature for a short time (several minutes). Thereby the intensity of its blue-violet hue is increased, because the inclusions of the original composition of cyclo-$Co_2P_4O_{12}$ are transformed into glassy products of the type $[Co(PO_3)_2]_n$. The composition of the pigment prepared under the conditions given can be roughly described by the formula $ZrSiO_4 . 0{\cdot}18[Co(PO_3)_2]_n$. Thus the content of expensive cobalt is relatively low compared with that in other cobalt pigments and is about 3% (w/w) of the pigment. When applied to glazes this represents as little as 0·09–0·21% (w/w) of the glaze.

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