Dyes and Pigments **14** (1990) 9–22

Synthesis of a Green–Blue Zirconium Silicate Pigment

M. Trojan

Institute of Chemical Technology, Legions Sq. 565, 532 10 Pardubice, Czechoslovakia

(Received 30 June 1989; accepted 10 August 1989)

ABSTRACT

A zirconium silicate pigment having an interesting green–blue hue has been synthesized. Its colour is based on the perturbation principle: vanadium ions, together with molybdenum ions, are incorporated into the zirconium silicate structure. A combination of disodium hexafluorosilicate, lithium hydroxide and sodium chloride proved useful as the mineralizer for the pigment synthesis. Further ingredients include molybdenum trioxide, which is a component of the mineralizer; in addition there is another important factor, which helps the chromophore to obtain the required greenish-blue hue. The effect of the V_2O_5 *content in the starting mixture on the colour of the pigment has been evaluated, and also the effect of* MoO_3*. The temperature conditions of the pigment synthesis have been established. The products have been evaluated from the standpoint of their structure, degree of conversion, colour hue, and ability to dye ceramic glazes.*

INTRODUCTION

The zirconium silicate (zircon) pigments represent a modern type of ceramic pigments of high quality. They exhibit high thermal, chemical and colour stability and can be used for colouring ceramic glazes. These pigments are based on the zirconium silicate formed during their synthesis and possessing the structure of zircon mineral.[1] Most usually they are 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 be coloured during the synthesis by two

Dyes and Pigments 0143-7208/90/$03·50

methods.[2] The first consists in the trapping of some ions in the silicate structure in the form of zirconium silicate pigments and is represented by the pigments coloured by the so-called inclusion method.[2,3] The inclusions are intensely coloured particles of compounds which are incorporated into the zircon microcrystals during their formation. There also exist zirconium silicate pigments (pink–violet,[4] brown–green[5,6] and blue–green[7]) which represent a combination of two methods of coloration, viz. defects and inclusion.

This paper demonstrates the possibility of the synthesis of zirconium silicate pigments which have a greenish-blue hue and which are based on the principles of structural defects.[8]

EXPERIMENTAL

The basic starting oxides for use in preparation of mixtures for synthesis of the pigment were: ZrO_2-7 (Goldschmidt, FRG) of 97·7% (w/w) purity[9] and SiO_2 from Austria.[9] These oxides are of natural origin and are used industrially for the syntheses of pigments of the zirconium silicate type.

When formulating the starting mixtures we adopted a previously suggested mineralizer which had proved useful in the syntheses of the zirconium silicate pigment.[10] This mineralizer contains Na_2SiF_6, LiOH, MoO_3 and NaCl. We also compared the effect of the amount of the molybdenum compound in the starting mixture. For the chromophore we selected vanadium pentoxide (V_2O_5). The effect of the amount of chromophore on the pigment quality was also assessed. The pigment based on zirconium silicate was initially a blue one, and the green–blue colour did not develop until above 1200°C. We therefore monitored the synthesis conditions with respect to the degree of conversion of the calcinate into the zirconium silicate and also to the pigment colour (after bisque firing) as a function of temperature and calcination time; in the second phase we followed the colour change to green–blue hue as a function of the temperature of the bisque firing. 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 monitored by thermal analysis[11] using a Derivatograph Q-1500 apparatus (MOM, Budapest). The mixtures were then calcinated at the selected temperature in porcelain crucibles in an electric resistance furnace. The calcinates were extracted with hot hydrochloric acid (1:1, v/v) to remove soluble residues of the mineralizer. The extracted calcinates were submitted to gravimetric analysis[12] to determine the content of pure zirconium silicate pigment.

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

RESULTS AND DISCUSSION

Thermal analysis of the starting mixtures

Thermal analysis (TA) provided information on the temperature regions of formation of the pigment investigated and on the effect of the mineralizer and chromophore components on the pigment synthesis (Fig. 1). After TA was completed, the samples were analysed[12] for $ZrSiO_4$ and/or the pigment content: see Table 1). Firstly, TA was applied to a mixture containing the basic oxides (ZrO_2 and SiO_2) together with two mineralizer components, Na_2SiF_6 and $LiOH.H_2O$ (curves B); MoO_3 was then added (curves C), and finally TA was applied to the complete starting mixture for the synthesis of the pigment investigated, i.e. with addition of NaCl and V_2O_5 (curve C_2 and C_5). (For the composition of mixtures B, C, C_2 and C_5 see Table 2.) The temperature was increased at a rate of 10°C min^{-1} during the TA, which corresponded to the rate of temperature increase in the electric resistance oven used for the subsequent calcinations. The TG curves show (above 100°C) a mass decrease corresponding to the release of a molecule of water of crystallization from lithium hydroxide [eqn (1)], the second and third decreases (at about 350–400°C and at about 500°C) being connected with release of 0·5 mol H_2O from LiOH due to a slow reaction with Na_2SiF_6 [eqn (2)] and the reaction with SiO_2 [eqn (3)]. The reaction of formation of zirconium silicate (see below) commenced at temperature (T_{R_1}) of 720–730°C in the B mixture, the relatively sharp maximum (T_m) of this exothermic process being observed at 790°C. When using MoO_3 in the starting mixture (C) the reaction is shifted to lower temperatures, its commencement and maximum being at 620–630 and 690°C, respectively. The exothermic effect is greater. The TG curve (C) from 500°C shows a slight mass decrease (greater than that of the B mixture); this is connected with a partial release of oxygen from MoO_3 [eqn (4)].[10] This oxygen, which is released in an active form, has distinct mineralization effects due to its high electronegativity. 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 the mixtures showed that an addition of chromophore (V_2O_5) will shift the

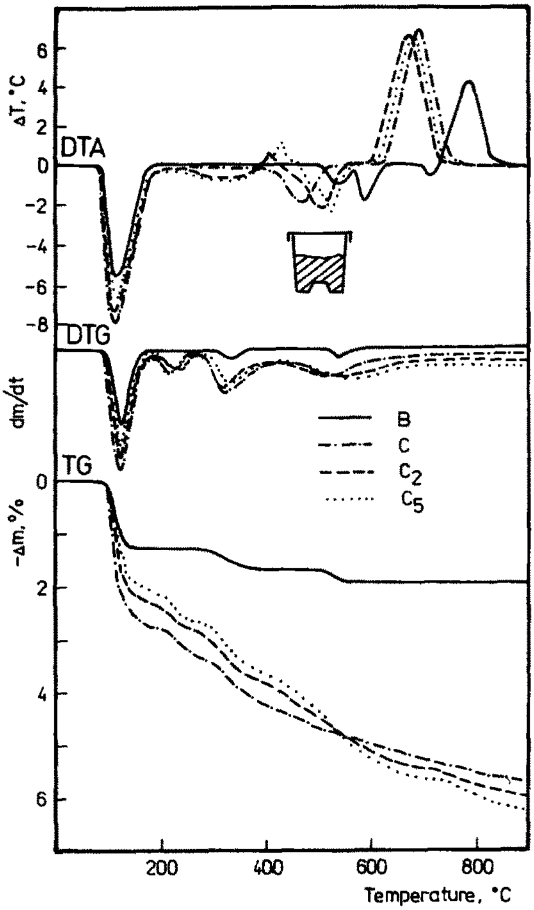

Fig. 1. Thermoanalytical curves of the starting mixtures B, C, C_2 and C_5 (see Table 2). Apparatus, Derivatograph Q-1500; temperature increase, 10°C min^{-1}; sample weight, 1000 mg; sensitivity of the balance, TG 100 mg, DTA 1/5, DTG 1/3; standard, α-Al_2O_3; atmosphere, air; platinum crucible with a lid.

exothermic effect of formation of zirconium silicate (the pigment) towards lower temperatures, viz. the beginning of the process (T_{R1}) 600°C (C_2) or 610°C (C_5) and the maxima of exothermic effects (T_m) at 670 and 680°C, respectively. Addition of the chromophore also increases the exothermicity of the process ($-\Delta H$) as well as its yields (i.e. the $ZrSiO_4$ or pigment content in the sample after TA—Table 1).

In the case of the C_5 mixture (i.e. that with a doubled amount of chromophore), the exothermicity and yields of the process are slightly lower than those of the C_2 mixture. The higher mass decrease of the thermoanalysed sample within the temperature interval above 400°C observed with the mixture containing the chromophore (as compared with

TABLE 1
Some Quantities Determined from TA for the Synthesis Reaction of $ZrSiO_4$ and/or Pigment

Mixture	T_{Ri} (°C)	T_m (°C)	$-\Delta H^{13}$ (kJ mol^{-1})	*Yield* (%)
B	730	790	13·8	61·8
M	630	690	20·6	82·6
C_2	600	670	19·3	80·9
C_5	610	680	18·2	79·6

the mixture without the chromophore, C) indicates a partial release of oxygen from V_2O_5 [eqn (5)]. This additional oxygen released in active form into the reaction mixture possesses, due to its great electronegativity, distinct mineralization effects. Therefore, the temperature of the pigment synthesis is further lowered. The greater amount of oxygen released from V_2O_5, compared with that released from MoO_3 (see the comparison of the TG curves for the C and C_5 mixtures), the smaller radius of the V^{4+} ion (compared with the Mo^{4+} ion) which enters the structure of the zirconium silicate formed instead of the much bulkier zirconium (see below), and the ability of vanadium oxide to move to the melt phase of vanadate bronzes, are responsible for the fact that the mineralization effects of V_2O_5 are greater than those of MoO_3. Therefore, with a doubled content of MoO_3 in the C_5 mixture, the mineralization efficiency of V_2O_5 is partially overshadowed; hence the reaction temperature increases slightly and the yields and exothermicity of the reaction will mildly decrease. (The increased MoO_3 content in the C_5 mixture is however necessary for the desirable green–blue colour hue to be reached in the final phase).

$$LiOH.H_2O = LiOH + H_2O \qquad (1)$$

$$6LiOH + Na_2SiF_6 = (M_2SiO_3) + 6MF + 3H_2O \ (M = Li, Na) \qquad (2)$$

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

$$MoO_3 = MoO_2 + \tfrac{1}{2}O_2 \qquad (4)$$

$$V_2O_5 = 2VO_2 + \tfrac{1}{2}O_2 \qquad (5)$$

The zirconium silicate itself (as the pigment basis) is formed in the following way. The lithium hydroxide reacts with the grains of starting silicon oxide [eqn (3)] and thus forces them to react in the synthesis of zirconium silicate [eqn (6)] [moreover, it partially decomposes Na_2SiF_6 into reactive intermediates; eqn (2)]. The presence of disodium hexafluorosilicate is important for starting the reaction of formation of the silicate. At the calcination temperature, by interaction with water vapour released from other reactions, the hexafluorosilicate is, to a smaller extent, also decomposed to sodium fluoride and silicium tetrafluoride [eqn (7)]. The gaseous SiF_4 represents a mobile and highly reactive component of the mixture, and it starts the mildly exothermic reactions of the synthesis of the silicate portions of the pigment [eqn (8)], these reactions also involving the alkali silicates [eqns (6) and (9)] formed by the reactions (2), (3) and (10).

$$(M_2SiO_3)_{(l)} + ZrO_{2(s)} + F_2 = ZrSiO_{4(s)} + 2MF_{(l)} + \tfrac{1}{2}O_2 \qquad (6)$$

$$Na_2SiF_6 = 2NaF + SiF_{4(g)} \qquad (7)$$

$$SiF_{4(g)} + ZrO_{2(s)} + O_2 = ZrSiO_{4(s)} + 2F_2 \qquad (8)$$

$$M_2SiO_{3(l)} + ZrO_{2(s)} + F_2 = ZrSiO_{4(s)} + (M_2O)_{(l)} + F_2 \qquad (9)$$

$$4MX_{(l)} + SiO_{2(s)} = 2(M_2SiO_3)_{(l)} + SiX_{4(g)} \qquad (10)$$

$$(M = Li, Na;\ X = F, Cl)$$

The melting temperatures of these silicates (if individual and pure) lie above the temperatures of formation of the pigment. In spite of that they are transferred, in the calcinated reaction mixture, into the melt layers at the surface of the grains of the basic oxides.[10] 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 pigment, a part of the transport of the silicon component is realized in the form of the reactive, gaseous SiF_4 or SiX_4,[14] which is formed in the mixture by decomposition of disodium hexafluorosilicate and by other reaction [eqn (10)]. In the reactions (8) of the formation of zirconium silicate, the fluorine released from the tetrahalide is extremely important for the synthesis of the zircon pigments. Due to their high electronegativity, the fluorine (and chlorine) atoms shield the strong repulsive forces[10,15] of silicon(IV) and zirconium(IV) ions, whereby their mutual approach, and consequently, reactions (6), (8) and (9) become possible. The reaction of formation of the zirconium silicate pigment can thus be expressed by eqns (11) and (12).

$$SiX_4 + (1-x-y)ZrO_2 + \frac{x}{2}V_2O_5 + yMoO_3 + \left(1 - \frac{x}{4} - \frac{y}{2}\right)O_2 = Zr_{1-x-y}V_x^{IV}Mo_y^{IV}SiO_4 + 2X_2 \qquad (11)$$

$$(M_2SiO_3) + (1-x-y)ZrO_2 + \frac{x}{2}V_2O_5 + yMoO_3 = Zr_{1-x-y}V_x^{IV}Mo_x^{IV}SiO_4 + M_2O + \left(\frac{x}{4} + \frac{y}{2}\right)O_2 \qquad (12)$$

The zirconium silicate pigment formed in this step is blue in colour. This colour is formed when vanadium ions are substituted in place of zirconium ions as uncharged structural defects. For the starting ZrO_2, which remains in the solid phase all the time, it can be suggested (in accord with our earlier reports[3]) that it is pulled into the reactions of pigment synthesis on the basis of transport of vacancies (v) in its defective crystal structure [eqns (13), (14) and (15)].

$$4MX + nZrO_2 = 4X_O^{\bullet} + v_{Zr}^{''''} + (n-1)ZrO_2 + 2M_2O \qquad (13)$$

$$4X_O^{\bullet} + v_{Zr}^{''''} + ZrO_2 + M_2O = 2M_{Zr}^{'''} + 3O_O^{x} + Zr_{Zr}^{x} + 3v_O^{\bullet\bullet} + X_2 \qquad (14)$$

$$2M_{Zr}^{'''} + 3O_O^{x} + Zr_{Zr}^{x} + 3v_O^{\bullet\bullet} + SiO_2 = ZrSiO_4 + M_2O \qquad (15)$$

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

Synthesis of the pigment

On the basis of the TA results we chose a temperature of 700°C and a time of 1 h for the subsequent calcination experiments, which was sufficient for the pigment synthesis. The pigment calcinates were prepared from the starting mixtures in which we varied the MoO_3 and V_2O_5 (chromophore) contents (Table 2). (Two basic starting oxides—ZrO_2 and SiO_2—and three basic mineralizer components—Na_2SiF_6, $LiOH.H_2O$ and NaCl—were always taken in constant amounts corresponding to the basic mixture B).

The calcinates were extracted with hot hydrochloric acid. The products

TABLE 2
Composition of the Basic Mixtures

Mixture	*Basic ingredients (g)*						
	ZrO_2	*SiO_2*	*Na_2SiF_6*	*$LiOH.H_2O$*	*NaCl*	*MoO_3*	*V_2O_5*
B	17·2	8·0	1·8	1·0	0·5	—	—
M	17·2	8·0	1·8	1·0	0·5	—	2·0
C	17·2	8·0	1·8	1·0	0·5	3·2	—

(A) Mixture Derived from the Basic Mixture M by Varying the MoO_3 Content

$M_1 = M + 1\,g\,MoO_3$
$M_2 = M + 2·1\,g\,MoO_3$
$M_3 = M + 3·2\,g\,MoO_3$
$M_4 = M + 4·3\,g\,MoO_3$
$M_5 = M + 5·5\,g\,MoO_3$
$M_6 = M + 6·7\,g\,MoO_3$

(B) Mixture Derived from the Basic Mixture C by Varying the Chromophore Content

$C_1 = C + 0·4\,g\,V_2O_5$
$C_2 = C + 0·8\,g\,V_2O_5$
$C_3 = C + 1·2\,g\,V_2O_5$
$C_4 = C + 1·6\,g\,V_2O_5$
$C_5 = C + 2·0\,g\,V_2O_5$
$C_6 = C + 2·4\,g\,V_2O_5$
$C_7 = C + 2·8\,g\,V_2O_5$
$C_8 = C + 3·2\,g\,V_2O_5$

Note: The mixtures M_3 and C_5 are identical.

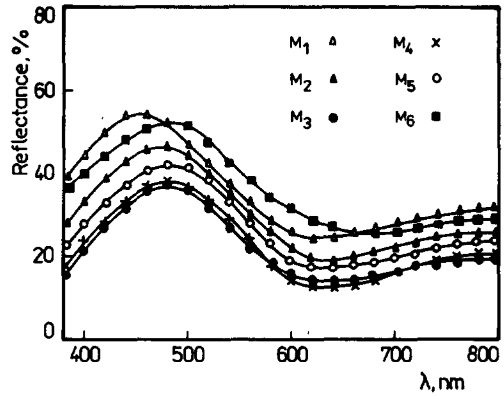

Fig. 2. Effect of the content of MoO_3 in the mixtures M_1–M_6 [see Table 2(A)] on the colour hue of the green–blue pigment (calcination conditions: 700°C for 1 h; bisque firing: 1450°C for 10 min).

obtained at this synthesis phase were blue. Only bisque firing (1450°C, 10 min) caused their colour to develop into a full green–blue hue [eqn (16)]

$$Zr_{1-x-y}V_x^{IV}Mo_y^{IV}SiO_4 = Zr_{1-x-y}V_{x-z}^{IV}V_z^{V}Mo_{y-z}^{IV}Mo_z^{III}SiO_4 \qquad (16)$$

The colour strength of the pigments thus prepared was measured (see Figs 2 and 3). The most intense green–blue hue was obtained with the mixture denoted as M_3 [Table 2(A)] whose composition is identical with that of mixture C_5 [Table 2(B)]. The composition of these mixtures was (in mass %): 51% ZrO_2, 23·8% SiO_2, 5·35% Na_2SiF_6, 2·95% $LiOH.H_2O$, 1·5%

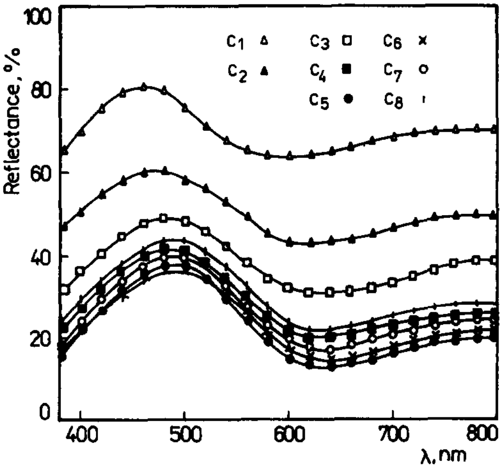

Fig. 3. Effect of the content of V_2O_5 chromophore in the mixtures C_1–C_8 [see Table 2(B)] on the colour hue of the green–blue pigment (calcination conditions: 700°C for 1 h; bisque firing: 1450°C for 10 min).

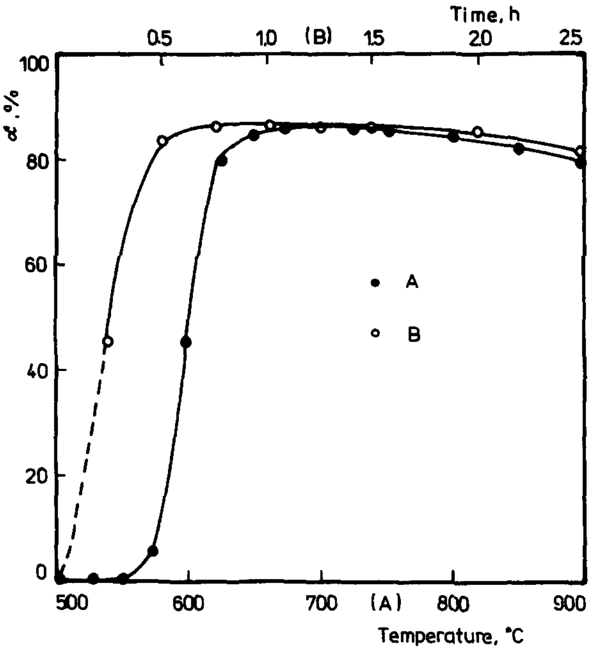

Fig. 4. Dependence of the degree of conversion (α) of the starting mixture M_3 [see Table 2(A)] to the green–blue pigment on calcination temperature (A, for a calcination time of 1·5 h, ●) and on calcination time (B, for a calcination temperature of 675°C, ○).

NaCl, 9·5% MoO_3 and 5·9% V_2O_5. Therefore, they were further used for the evaluation of the other conditions of the pigment synthesis, its quality and application properties.

In the calcination temperature region of 500–900°C (calcination time of 1·5 h) we studied the extent of conversion of the extracted calcinates (HCl, 1:1, v/v) into the pigment (still in a blue hue state at this phase). From curve A (Fig. 4) it follows that the first portions of zirconium silicate begin to appear in the reaction mixture above a temperature of 575°C, the degree of conversion being sufficient (almost 80%) at temperatures above 625°C. Under these conditions the optimum calcination temperature lay at 650–750°C when the pigment content in the extracted calcinate exceeded 85%. It was found, however, that further increase of the calcination temperature decreased the degree of conversion slightly. This can be explained by the relatively high content of a strongly alkaline melt phase in the calcinated mixture, which causes, after completion of the synthesis of the pigment, its subsequent decomposition [eqns (17) and (18)], especially at enhanced calcination temperatures.

$$(M_2O) + ZrSiO_4 = M_2ZrSiO_5 \qquad (17)$$

$$(M_2O) + M_2ZrSiO_5 = M_2ZrO_3 + M_2SiO_3 \qquad (18)$$

At 675°C, the time dependence of the degree of conversion of the calcinates was also determined. From Fig. 4, curve B, it follows that a period of 30–45 min is sufficient at this calcination temperature. Above 1·5–2 h of calcination, the degree of conversion is slightly decreased, which is again connected with the influence of the aggressive alkaline melt on the calcinate, the product being slowly decomposed during prolonged calcination [eqns (17) and (18)].

The pigment prepared at the optimum conditions (i.e. the M_2 composition of the starting mixture, 675°C, calcination time 1 h), and still in a blue hue state at this phase, was purified by extraction with hot acids (HF and H_2SO_4)[12] and analysed. X-Ray diffraction analysis confirmed that the pigment structure corresponded to that of the zircon mineral, i.e. the tetragonal space-centred lattice.[1,10] Electron microscopy also confirmed the compactness of the pigment particles and did not record any other type of particles; their magnitude varied around 5 μm, which generally corresponds to pigments of zirconium silicate type.[10] The structural parameters of the pigment, when blue-coloured (i.e. not fired), are $a_0 = 0{\cdot}660\,71$ nm and $c_0 = 0{\cdot}598\,08$ nm. Hence they are slightly less than in the case of the pure zirconium silicate prepared synthetically.[10,16] This is due to the fact that two ions which are incorporated into the zircon structure of the silicate as substitution defects instead of zirconium have a smaller radius than the ion of four-valent zirconium.[17] These are the ions of vanadium and molybdenum. In the case of these ions it is possible to presume that they will enter the pigment structure in the four-valent state, i.e. as uncharged defects V_{Zr}^{x} and Mo_{Zr}^{x}.

The blue pigment had to be transformed into a green–blue one by bisque firing at high temperatures. Therefore, the product prepared under the optimum conditions (the M_3 mixture, 675°C, 1 h) and extracted with HCl (1:1, v/v) was submitted to the bisque firing at 1200–1500°C, when the pigment obtained its final green–blue hue [eqn (16)]; 10 min was sufficient. The intensity of its green component hue increased with the temperature of the bisque firing (Fig. 5) up to a maximum at 1450°C; from this standpoint, these temperatures can be considered as the optimum. At higher temperatures of bisque firing the intensity of the green hue slowly decreases. Electron microscopy showed that the bisque firing does not cause any damage to the surface of the pigment microcrystals. (Only their rounded-off edges above 1450°C indicate partial melting.) The structure of the pigment and its structural parameters did not change significantly during the bisque firing, which was expected ($a_0 = 0{\cdot}660\,74$ nm, $b_0 = 0{\cdot}598\,20$ nm). The reason for the green–blue coloration of the pigment obtained during the bisque firing at high temperatures can be explained as follows. The vanadium and molybdenum ions present as substitution defects in the zirconium silicate

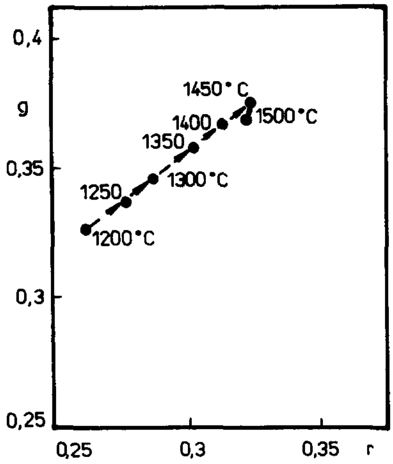

Fig. 5. The change in colour intensity of the green–blue pigments (rgb system) with the temperature of bisque firing.

structure obviously undergo a change in valence at the extreme conditions of bisque firing (in order to retain the condition of electroneutrality, their charge is also changed). A part of the tetravalent vanadium ions changes to the pentavalent form (this causes a little green colouration) and an equivalent part of the tetravalent molybdenum ions must be changed to a lower valence state. Thus they are converted to a state in which they represent charged defects, viz.—$V_{Zr}^{\bullet}$, and Mo_{Zr}'. Obviously this state is somewhat less stable. This was confirmed by a long-term (several days) calcination of the green–blue pigment at temperatures about 1350°C, when a partial decrease of intensity of the green hue was observed; the ion-defects probably begin to return to their original more stable state. The stability of the green–blue colour is sufficient, since the temperatures and times of glazing are lower in the industrial production of standard ceramic glazes.

With the aim of confirming the above observations on the reason for the colour of this zircon pigment, we investigated the use of alternatives to the two components of the reaction mixture. In the first case lithium hydroxide was replaced by sodium hydroxide (in an amount corresponding by weight to two-thirds of the LiOH moles) in the mixtures M_1 and M_2.

With the application of synthesis temperatures in the range 600–750°C it was shown that the M_1 mixture (with 0·67 g NaOH) gives an only pale blue pigment below 700°C (the degree of conversion was 54·2% at 700°C). At a temperature of 750°C the degree of conversion was sufficient (86·7%) and the pigment was an intensive blue colour. After bisque firing at 1450°C, however, this colour hue did not change significantly. The M_3 mixture (with 2·13 g NaOH) was sufficiently reacted at 700°C (80·5%) and the pigment had an intensive blue colour; its bisque firing at 1450°C produced the green–blue hue. Hence it would be possible to replace the mineralizer component $LiOH.H_2O$ by the cheaper NaOH. However, the synthesis temperature has to be increased by almost 100°C, and the intensity of the green component of the pigment is weaker. In the second case we replaced molybdenum trioxide, in the mixture M_3, by ammonium dodecatungstate or cryolite (Na_3AlF_6). After 2 h calcination at 750°C (degree of conversion above 80%), the product was submitted to bisque firing at 1450°C to give (when ammonium dodecatungstate had been used) a pigment of an intense greenish-blue colour. This product was similar to the best pigments prepared from mixtures containing MoO_3 (the M_3 mixture, the optimum conditions of calcination and bisque firing). The possibility of replacing molybdenum ions by tungsten ions agrees with the above conclusions that the colouring defects in the zircon pigment are predominantly the vanadium ions; without them it is impossible to prepare this pigment. When cryolite was used in place of MoO_3 the resultant pigment was of an interesting greyish-blue colour. The grey colour is caused by the incorporation of aluminium ions into the zircon structure and the greenish-blue hue was not formed at all.

The optimum temperature conditions of the synthesis of this green–blue pigment were confirmed by the above-mentioned degree of conversion of the calcinate into the pigment, and also by the colour hue of the pigments (after bisque firing at 1450°C) as well as that of the ceramic glazes containing these

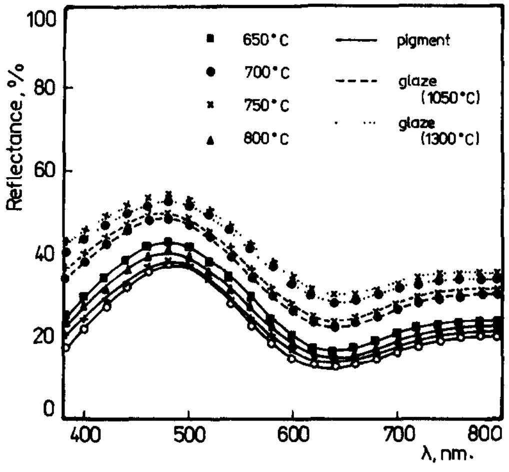

Fig. 6. The colour hue of the green–blue pigments (——), synthesized from the mixture M_3 [see Table 2(A)] at temperatures 650°C (■), 700°C (●), 750°C (×) and 800°C (▲) (calcination time 1 h) after bisque firing at 1450°C; of middle-temperature glaze (temperature of glazing 1050°C, ---); and of high-temperature glaze (1300°C, ······), with 10% (w/w) pigments.

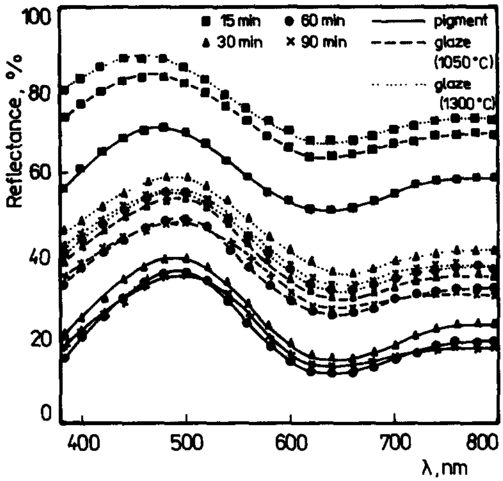

Fig. 7. The colour hue of the green–blue pigments (——) synthesized by the mixture and at calcination time 15 min (■), 30 min (▲), 60 min (●) and 90 min (×) (for temperature 700°C); of middle-temperature glaze (temperature of glazing 1050°C, – – –); and of high-temperature glaze (1300°C, ······), with 10% (w/w) pigments.

pigments (Figs 6 and 7). The most intense green–blue pigment can be obtained from the M_3 mixture at synthesis temperatures of 675–750°C maintained for 0·5–1 h. Its application to a medium-temperature borate–silicate glaze (glazing temperature 1050°C) gives the same colour hue in the glaze. The same result was also obtained from application of the pigment to a high-temperature silicate glaze (glazing temperature 1300°C). This confirms the good thermal stability of the pigment which is quite sufficient for all ceramic glazing purposes.

CONCLUSION

The green–blue zirconium silicate pigment is best prepared by the procedure suggested in this communication from the starting mixture (M_3) containing (%, w/w): 51 ZrO_2, 23·8 SiO_2, 5·35 Na_2SiF_6, 2·95 $LiOH.H_2O$, 1·5 NaCl, 9·5 MoO_3 and 5·9 V_2O_5. The calcination temperature and time are advantageously 675–700°C and 0·5–1 h, respectively. After an extraction with diluted HCl, the colourless calcinate is submitted to a short (about 10 min) bisque firing at about 1450°C to produce an intense green–blue pigment. The pigment exhibits high thermal and chemical stability and can be applied to all types of ceramic glazes including the high-temperature ones (with glazing temperatures of 1300°C). When used in an amount of 3–10% (w/w) it effectively imparts the same green–blue hue to these glazes. The coloured glazes are smooth, glossy, and without any surface unevenness.

REFERENCES

1. Demiray, T., Nath, O. K. & Hummel, F. A., *J. Am. Ceram. Soc.*, **53** (1970) 1.
2. Broll, A., Beyer, H. A. & Kleinschmit, P., *Chem. Ztg*, **101** (1977) 319.
3. Trojan, M., *Dyes and Pigments*, **9** (1988) 221, 261, 324.
4. Trojan, M. & Pecárová, K., Czech. Patent 243 747 (1985).
5. Trojan, M., Czech. Patent 246 786 (1986); Czech. Patent Application 08712-88 (1988).
6. Trojan, M., *Scientific Papers, Inst. Chem. Technol., Pardubice*, **52** (1988) 265.
7. Trojan, M., Czech. Patent Application 08710-88 (1988).
8. Trojan, M., Czech. Patent 240 724 (1985).
9. Trojan, M. & Šolc, Z., *Silikáty*, **28** (1984) 22.
10. Trojan, M. & Šolc, Z., *Proc. ZIRCONIA '86 Tokyo II*, Uchida Rokakuho Publ. Co., Tokyo, 1987, p. 335.
11. Trojan, M. & Šolc, Z., *Supplement Proc. Conf. VIII ICTA, Bratislava 1985*, p. 57.
12. Trojan, M., Czech. Patent 233 691 (1984); *idem*, *Chem. Listy*, **80** (1986) 640.
13. Pillojan, G. O., *Vvedenije v Teoriju Terminičeskovo Analiza.* Izd. Akad. Nauk, Moscow, 1984, p. 232.
14. Eppler, R. A., *Ceram. Bull.*, **56** (1977) 213.
15. Hibino, T., Yamazaku, T. & Sekyia, H., *Kogyo Kagaku Zasshi*, **69** (1966) 2098.
16. Trojan, M., *Steklo Keram.*, **8** (1988) 29.
17. Liebau, F., *Structural Chemistry of Silicates*, Springer-Verlag, Berlin, Heidelberg, 1985, p. 410.