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A Brown Zirconium Silicate Pigment

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ABSTRACT

A zirconium silicate pigment in a new hue—brown—has been synthesized. Its colour is based on the perturbation principle: tellurium ions, together with lithium and molybdenum (or tungsten) ions, are incorporated into the zirconium silicate structure. A combination of disodium hexafluorosilicate and lithium hydroxide proved useful as the mineralizer for the pigment synthesis. Alkali or ammonium tellurate (K_2TeO_4 *was used in this work) acts as the chromophore. Further ingredients include molybdenum trioxide (ammonium molybdate can also be used) or ammonium paratungstate (*WO_3 *is also useful), which are components of the mineralizer and also the chromophore. The effect of the* K_2TeO_4 *content in the starting mixture on the colour of the pigment has been evaluated, together with the effect of* MoO_3 *and ammonium paratungstate. The temperature conditions of the pigment synthesis have been established and the products have been evaluated from the standpoint of their structure, conversion degree, colour hue and ability to colour ceramic glazes.*

1 INTRODUCTION

The zirconium silicate (zircon) 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 all types of ceramic glazes. These pigments are based on the zirconium silicate formed during their synthesis and possess the structure of zircon mineral.[1] Most usually they are prepared

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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 ways.[2]

The first way consists of the trapping of some ions in the silicate structure in the form of colouring defects.[1,3–5] The best known representatives of this group are the blue pigment[3,6] $Zr_{1-x}V_xSiO_4$ and the yellow pigment[4] $Zr_{1-x}Pr_xSiO_4$. Their colour is due to uncharged substitution defects of four-valent vanadium ions or praseodymium ions instead of zirconium[3–6] (V_{Zr}^{x} or Pr_{Zr}^{x}). The second group of zirconium silicate pigments is represented by the pigments coloured by so-called inclusion.[2,3–5] The inclusions are intensely coloured particles of some compounds which are incorporated into the zircone microcrystals during their formation. The protective layer of zirconium silicate covering these particles then serve in the subsequent application as a protection against aggressive glaze melt. The particles alone would not resist this medium and would not retain their colouring ability. Known pigments of this type include: e.g., the pink pigment[2,5,7] $ZrSiO_4 . x\ \alpha\text{-}Fe_2O_3$; the orange pigment[2,8] $ZrSiO_4 . xCd(S,Se)$ pigment; or the blue-violet pigment $ZrSiO_4 . x/Co(PO_3)_2/n$ developed in our laboratory.[9]

Also developed in our laboratory was the brown-green zirconium silicate pigment which is coloured on the basis of combination of the perturbation and inclusion principles.[10] However, no purely brown zirconium silicate pigment has been prepared until now.[11] It is described in this present report.

2 EXPERIMENTAL

The basic starting oxides for use in the preparation of the mixtures for synthesis of the pigment were: ZrO_2-7 (Goldschmidt) of 97·7% (w/w)[6] purity and SiO_2 from Austria.[6] These oxides, of natural origin, are used industrially for the synthesis of pigments of the zirconium silicate type.

When composing the starting mixtures we utilized the previously suggested mineralizer which has proved useful in the synthesis of the zirconium silicate pigments.[12] This mineralizer contains Na_2SiF_6, LiOH and molybdenum (VI) oxide or ammonium or alkali salts. We also compared the effects of the amount of the molybdenum (tungsten) compound in the starting mixtures. For the chromophore we selected potassium (I) tellurate (VI)—K_2TeO_4. The effect of the chromophore amount on the pigment quality was also studied. The pigment based on zirconium silicate was synthesized initially as colourless (white), and its brown colour did not develop until above 1200°C. Therefore we monitored the synthesis conditions by the conversion degree of the calcinate into the zirconium silicate and also according 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 a brown 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 followed by thermal analysis[13] using a derivatograph Q-1500 apparatus (MOM, Budapest). The mixtures were then calcinated at a chosen 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 pigments was evaluated by measurements of spectral reflectance in the visible region using a Specol 10 apparatus with an R 45/0 reflectance adapter (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).

3 RESULTS AND DISCUSSION

3.1 Thermal analysis of the starting mixtures

Thermal analysis (TA) provided information about the temperature regions of formation of the pigment investigated and about the effect of the mineralizer and chromophore components on the pigment synthesis (Fig. 1). (The samples after the completed TA were also analysed[14] for the $ZrSiO_4$ and/or the pigment content—Table 1). Firstly, the TA was applied to a mixture containing the basic oxides (ZrO_2 and SiO_2) together with two

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

Mixture	T_{Ri} (°C)	T_m (°C)	$-\Delta H^{15}$ (kJ mol^{-1})	*Yield* % α
B	720–730	790	13·8	61·8
M	620–630	690	20·6	82·6
C_2	780	820	15·6	74·0
C_4	800	840	14·2	68·3

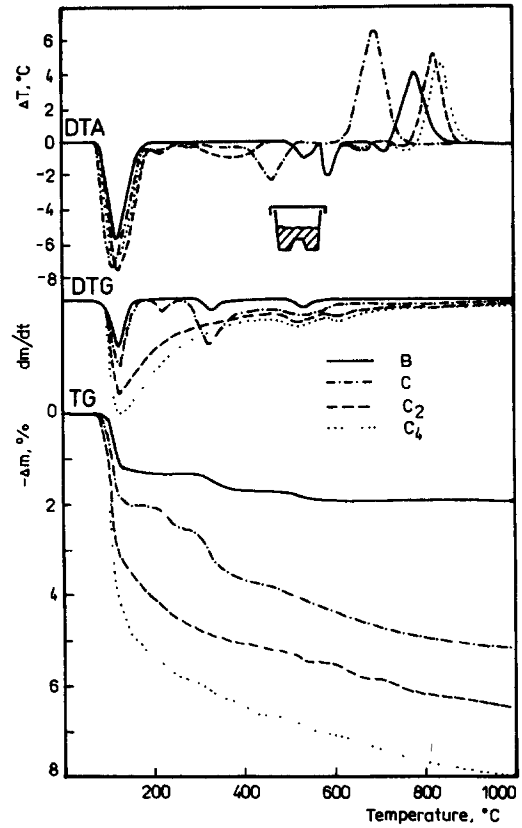

Fig. 1. Thermoanalytical curves of the starting mixtures B, C, C_2 and C_4 (see Tables 2 and 3). Apparatus, derivatograph Q-1500; temperature increase, 10°C min^{-1}; sample weight, 1000 mg; sensitivity of the balance TG 100 mg, DTA 1/5, DTG 1/3; standard, α-Al_2O_3; atmosphere, air; Pt-crucible with a lid.

mineralizer components—Na_2SiF_6 and $LiOH.H_2O$ (curve B, Fig. 1), then MoO_3 was added (curve C), and finally TA was applied to the complete starting mixture for the synthesis of the pigment investigated, i.e. with addition of the chromophore K_2TeO_4 11·94% and 21·33%—curves C_2 and C_4. (For the composition of mixtures B, C, C_2 and C_4, see Tables 2 and 3.) The temperature was increased at a rate of 10°C per min during the TA, which corresponds to the temperature increase used in the electric resistance oven used for the subsequent calcinations.

The TG curves (in Fig. 1) show that above 100°C, a mass decrease occurs corresponding to the release of a molecule of water of crystallization from lithium hydroxide:

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

TABLE 2
Composition of the Basic Mixtures under Evaluation and the Mixtures Derived from the Basic Mixture M by Varying the MoO_3 Content

Basic mixture (g)	*ZrO_2*	*SiO_2*	*Na_2SiF_6*	*$LiOH.H_2O$*	*MoO_3*	*K_2TeO_4*
B	16	8	2	1·5	—	—
M	16	8	2	1·5	—	4
C	16	8	2	1·5	2	—

Derived mixtures

$M_1 = M + 1gMoO_3$
$M_2 = M + 2gMoO_3$
$M_3 = M + 4gMoO_3$
$M_4 = M + 6gMoO_3$
$M_5 = M + 8gMoO_3$
$M_6 = M + 10gMoO_3$
$M_7 = M + 12gMoO_3$
$M_8 = M + 16gMoO_3$

TABLE 3
The Mixtures Derived from the Basic Mixture C by Varying the Chromophore (K_2TeO_4) *Content*

$C_1 = C + 2gK_2TeO_4$
$C_2 = C + 4gK_2TeO_4$
$C_3 = C + 6gK_2TeO_4$
$C_4 = C + 8gK_2TeO_4$
$C_5 = C + 10gK_2TeO_4$
$C_6 = C + 12gK_2TeO_4$
$C_7 = C + 16gK_2TeO_4$
$C_8 = C + 24gK_2TeO_4$

For basic mixture C composition, see Table 2.

the second and third decrease (about 350–400°C and about 500°C) being connected with the release of 0·5 mol of water from LiOH due to the slow reaction with Na_2SiF_6 (eqn (2)) and the reaction with SiO_2 (eqn (3))

$$6LiOH + Na_2SiF_6 = (M_2SiO_3) + 6MF + 3H_2O \quad (M = Li, Na) \tag{2}$$

$$2LiOH + SiO_2 = (Li_2SiO_3) + H_2O \tag{3}$$

The reaction of formation of zirconium silicate (see below) itself starts from a temperature (T_{Ri}) of 720–730°C in mixture B and the relatively sharp maximum (T_m) of this exothermic process was found at 790°C.

When using MoO_3 in the starting mixture (mixture C) this reaction is somewhat shifted to lower temperatures; its initial and maximum temperatures being at 620–630 and 690°C, respectively. The exothermic effect is greater. The TG (curve C) from 500°C shows a mild mass decrease (greater than that of mixture B); this is connected with a partial release of oxygen from MoO_3.[12]

$$MoO_3 = MoO_2 + \tfrac{1}{2}O_2 \tag{4}$$

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 finished TA (Table 1) increases, too. Thermal analysis of the mixtures showed that an addition of chromophore (K_2TeO_4) will shift the exothermic effect of formation of zirconium silicate (the pigment) toward higher temperatures, viz., the beginning of the process (T_{Ri}) 780°C (C_2) or 800°C (C_4), the maxima of exothermic effects (T_m) at 820 and 840°C, respectively. Addition of the chromophore lowers 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)). This means that the tellurate has negative effects from the standpoint of the mineralization of zirconium silicate as the basis of the pigment. This can be explained by the fact that, during calcinations of the mixtures with the chromophore, oxygen is also released from K_2TeO_4

$$TeO_4^{2-} = TeO_3^{2-} + \tfrac{1}{2}O_2 \tag{5}$$

$$TeO_3^{2-} = TeO_2^{2-} + \tfrac{1}{2}O_2 \tag{6}$$

but this happens at a lower temperature than those suitable for the synthesis of $ZrSiO_4$ (see the C_2 and C_4 TG curves and compare with the C curve). At the moment of formation of $ZrSiO_4$ as the basis of the pigment, this oxygen is not available for the reverse oxidation of tellurium ions to the four-valent form in which they enter the $ZrSiO_4$ lattice.

$$TeO_2^{2-} + \tfrac{1}{2}O_2 = TeO_2 + O^{2-} \tag{7}$$

On the other hand, this reaction also consumes the oxygen released from MoO_3 by eqn (4). However, the K^+ ions from the chromophores can also contribute to a lowering of the mineralization effects: they shift the temperature of formation of the melt phase (formed between the SiO_2 and ZrO_2 grains) to higher values as can be seen by the endothermic effect at the temperature curve of DTA at 650°C compared with the corresponding effects at curves B and C of DTA at 500 and 550°C, respectively.

The zirconium silicate itself (as the pigment basis) is formed in the following way. The lithium hydroxide reacts with the grains of starting silicium oxide, see eqn (3), and thus forces them to react in the synthesis of zirconium silicate.

$$(M_2SiO_3)_{(l)} + ZrO_{2(s)} + F_2 = ZrSiO_{4(s)} + 2MF_{(l)} + \tfrac{1}{2}O_2 \tag{8}$$

Moreover, it partially decomposes Na_2SiF_6 into reactive intermediates, see eqn (2). The presence of disodium hexafluorosilicate is important for starting the reaction of formation of the silicate. By the action of the calcination temperature in conjunction with the water vapour released in some of the reactions, the hexafluorosilicate is, to a lesser extent, also decomposed to sodium fluoride and silicium tetrafluoride.

$$Na_2SiF_6 = 2NaF + SiF_4 \qquad (9)$$

The gaseous SiF_4 represents a mobile and highly reactive component of the mixture, and it starts the mildly exothermic reaction of the synthesis of the silicate portions of the pigment, see eqn (10), which also involves the alkali silicates (see eqns (8) and (11)) formed by the reactions shown in eqns (2), (3) and (12).

$$SiF_{4(g)} + ZrO_{2(s)} + O_2 = ZrSiO_{4(s)} + 2F_2 \qquad (10)$$

$$M_2SiO_{3(l)} + ZrO_{2(s)} + F_2 = ZrSiO_{4(s)} + (M_2O)_{(l)} + F_2 \qquad (11)$$

$$4MF_{(l)} + 3SiO_{2(s)} = 2(M_2SiO_3)_{(l)} + SiF_{4(g)} \qquad (12)$$

$$(M = Li, Na, (K))$$

The melting temperatures of these silicates (as pure single compounds) 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.[12] Thus they become mobile components in the mixture and contribute to the transport between the reaction components. However, at the temperature of the synthesis of the pigment, a part of transport of the silicium component is realized in the form of the reactive gaseous SiF_4[16] which is formed in the mixture by decomposition of disodium hexfluorosilicate and by the reaction shown in eqn (12). In the reaction of formation of zirconium silicate, shown in eqn (10), the fluorine released from the tetrahalogenide is extremely important for the synthesis of zircone pigments. Due to their high electronegativity, the fluorine atoms shield the strong repulsive forces[12,17] of silicon (IV) and zirconium (IV) ions, whereby their mutual approach and the reactions shown in eqns (8), (10) and (11) are made possible.

For the starting ZrO_2, which remains in the solid phase all the time, it can be suggested (in accordance with our earlier reports)[3-5] that it is pulled into the reaction of the pigment synthesis on the basis of transport of vacancies in its defective crystal structure:

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

$$4F_O^{\bullet} + v_{Zr}^{''''} + ZrO_2 + M_2O = 2M_{Zr}^{'''} + 3O_O^{x} + Zr_{Zr}^{x} + 3v_O^{\bullet\bullet} + F_2 \qquad (14)$$

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

$$(M = Li, Na\ (K))$$

3.2 Synthesis of the pigment

On the basis of the TA results we chose a temperature of 850°C and a time of 1·5 h for the subsequent calcination experiments, these conditions being

TABLE 4

The Mixtures Derived from the Basic Mixture B by Varying the MoO_3 and the Chromophore Content

$MC_1 = B + 1gMoO_3 + 3gK_2TeO_4$
$MC_2 = B + 1gMoO_3 + 4gK_2TeO_4$
$MC_3 = B + 1gMoO_3 + 5gK_2TeO_4$
$MC_4 = B + 2gMoO_3 + 3gK_2TeO_4$
$MC_5 = B + 2gMoO_3 + 4gK_2TeO_4$
$MC_6 = B + 2gMoO_3 + 5gK_2TeO_4$
$MC_7 = B + 3gMoO_3 + 3gTeO_4$
$MC_8 = B + 3gMoO_3 + 4gK_2TeO_4$
$MC_9 = B + 3gMoO_3 + 5gK_2TeO_4$

For basic mixture B composition, see Table 2.
The mixtures M_2 (Table 2), C_2 (Table 3) and MC_5 (Table 4) are identical.

sufficient for the pigment synthesis. The pigment calcinates were prepared from the starting mixtures in which the MoO_3 and K_2TeO_4 (chromophore) contents were varied (Tables 2–4). Two basic starting oxides, ZrO_2 and SiO_2, and two basic components of the mineralizer, Na_2SiF_6 and $LiOH.H_2O$, were always taken in constant amounts corresponding to the basic mixture B.

The calcinates were extracted with hot hydrochloric acid. The products obtained at this synthesis phase were practically colourless (white). Only their bisque firing (1400°C, 10 min) caused their colouration to give a full brown hue.

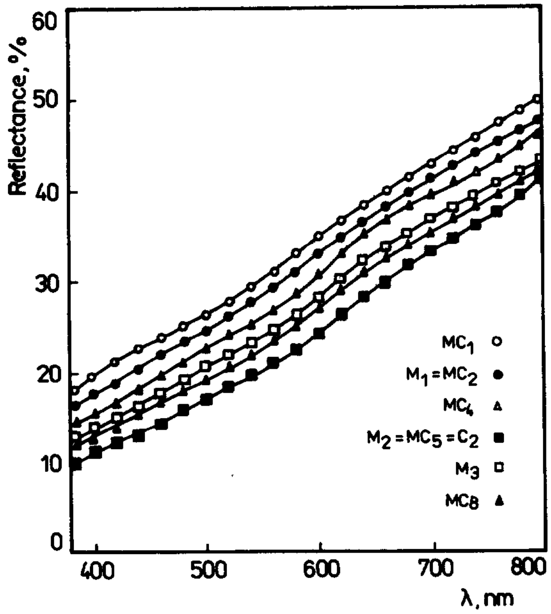

Fig. 2. The influence of various contents of MoO_3 and K_2TeO_4 in mixtures M and MC (see Tables 2 and 4) on the colour hue of brown pigments (calcinated to 850°C for 1·5 h).

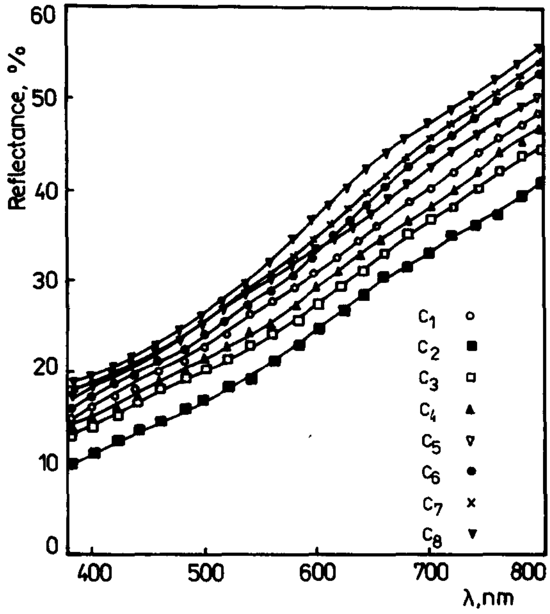

Fig. 3. Effect of the content of chromophore K_2TeO_4 in the mixtures C_1–C_8 (see Table 3) on the colour hue of the brown pigment (the conditions: 850°C for 1·5 h; the bisque firing: 1400°C for 10 min).

The colour strength of the pigments thus prepared was measured (see Figs 2 and 3). The most intense brown hue was obtained with the mixture denoted as M_2 (Table 2), the composition of which is identical to that of mixture C_2 (Table 3) and MC_5 (Table 4). The composition of this mixture is (in mass %): 47·76% ZrO_2, 23·88% SiO_2, 5·97% Na_2SiF_6, 4·48% $LiOH.H_2O$, 5·97% MoO_3, 11·94% K_2TeO_4. Therefore, this mixture was used further for evaluation of the other conditions of the pigment synthesis, its quality and application properties.

In the calcination temperature region of 650 to 1000°C (calcination time of 1·5 h) we followed the extent of conversion of the extracted calcinates (HCl 1:1) into the pigment (in colourless 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 675°C, the conversion degree being sufficient (almost 80%) at temperatures above 775°C. Under these conditions, the optimum calcination temperature lies between 800 and 850°C when the pigment content in the extracted calcinate exceeds 85%. It was found, however, that further increase of the calcination temperature decreases the conversion degree slightly. This finding can be explained by the relatively high content of strongly alkaline melt phase in the calcinated mixture, which causes, after the completed synthesis of the pigment, its

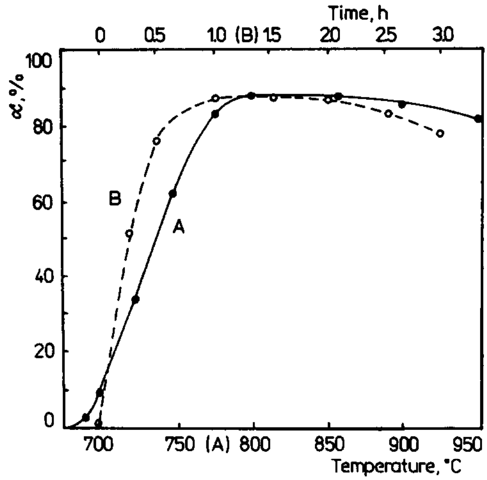

Fig. 4. The dependence of the conversion degree (α) of the starting mixture M_2 (C_2, MC_5)—see Tables 2–4, to brown pigment—on the calcination temperature (A, for the calcination time of 1·5 h) and on the calcination time (B, for the calcination temperature of 850°C).

subsequent decomposition, see eqns (16) and (17), especially at enhanced calcination temperatures.

$$(M_2O) + ZrSiO_4 = M_2ZrSiO_5 \qquad (16)$$

$$(M_2O) + M_2ZrSiO_5 = M_2ZrO_3 + M_2SiO_3 \qquad (17)$$

At 850°C, the time dependence of the conversion degree of the calcinates was also determined. From Fig. 4, curve B it follows that the period of 1 h is sufficient at this calcination temperature. Above 2 h calcination, the conversion degree 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, see eqns (16) and (17).

The pigment prepared at the optimum conditions—the M_2 composition of the starting mixture, 850°C, calcination time 1·5 h (still in a colourless state at this phase) was purified by extraction with hot acids (HF and H_2SO_4)[14] and analysed. X-ray diffraction analysis confirmed a pigment structure corresponding to that of the zircon mineral, i.e., the tetragonal space-centered lattice.[1,12] Electron microscopy also confirmed the compactness of the pigment particles and did not record any other type of particles; their magnitude varied within the limits 3 to 7 μm, which generally corresponds to pigments of the zirconium silicate type.[12]

The structural parameters of the colourless pigment are: $a_o = 0{\cdot}660\,53(5)$ nm and $c_o = 0{\cdot}598\,31(6)$ nm ($c/a = 0{\cdot}905\,8(5)$, and the volume of the elementary unit cell $V = 0{\cdot}261\,04(5)\,\mathrm{mm}^3$).

These values are slightly lower than in the case of the pure zirconium silicate prepared synthetically.[10,18] This is because the three ions which were 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.[19] These include the ions of tellurium, molybdenum and, of the three alkali ions present in the reaction mixture, predominantly lithium, which are of the smallest magnitude. The lithium ions produce negatively charged defects $\mathrm{Li}'''_{\mathrm{Zr}}$ in the structure of zirconium silicate. The strongly negative charge of these defects is compensated by a partial inclusion of fluoride ions in the places of the oxygen ions[12]—the positively charged substitution defects—$\mathrm{F}^{\bullet}_{\mathrm{O}}$. In the case of tellurium and molybdenum ions it is possible to presume, on the basis of TA, that they will enter the pigment structure in the four-valent state, i.e. as uncharged defects $\mathrm{Te}^{x}_{\mathrm{Zr}}$ and $\mathrm{Mo}^{x}_{\mathrm{Zr}}$.

The colourless pigment had to be transformed into a coloured one by bisque firing at high temperatures. Therefore, the product prepared under the optimum conditions (the M_2 mixture, 850°C, 1·5 h) and extracted with HCl 1:1 was submitted to bisque firing at 1200–1500°C, when the pigment obtained (10 min was sufficient) its final brown hue. The intensity of its brown colour increased with the temperature of the bisque firing (Fig. 5) up to a maximum at 1350 and 1400°C; from this standpoint, these temperatures can be considered the optimum. At higher temperatures of bisque firing the colour intensity slowly decreases. Electron microscopy showed that the bisque firing does not cause any damage to the integrity or surface of the pigment microcrystals. (Rounded-off edges above 1450°C indicate partial melting.) Also the structure of the pigment and its structural parameters did not practically change during the bisque firing, which was as expected ($a_o = 0{\cdot}660\,50(3)$ nm, $b_o = 0{\cdot}598\,35(3)$ nm, $c/a = 0{\cdot}905\,9(3)$, $V = 0{\cdot}261\,02(4)\,\mathrm{nm}^3$). The reason for the brown colour of the pigment, obtained during the bisque firing at high temperatures can be explained as follows. The tellurium and molybdenum ions present as substitution defects in the zirconium silicate structure obviously undergo a change in valency at the extreme conditions of bisque firing (in order to retain the condition of

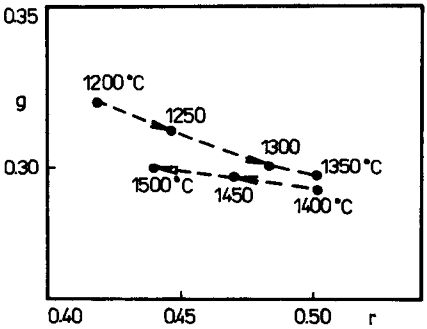

Fig. 5. The change in colour intensity of brown pigments (RGB system) caused by various temperatures of the bisque firing.

electroneutrality, their charge is also changed). Thus they are converted to a state in which they represent colouring defects (especially so the tellurium ions). Obviously this state is somewhat less stable. This was confirmed by a long-term (several days) calcination of the brown pigment at about 1350°C, when a partial decrease of intensity of the brown hue is observed; the ion defects probably begin to return to their original more stable state. The stability of the brown colour is sufficient, since the temperatures and times of glazing are lower in industrial or usual ceramic glazes.

With the aim of confirming the above-suggested principle of the colour origin of the brown zircon pigment, we carried out substitutions of two of the components of the reaction mixture. In the first case lithium hydroxide was replaced by sodium hydroxide. Although at the synthesis temperatures of 900 and 950°C (maintained for 2 h) we achieved the conversion of the reaction mixture into zirconium silicate (about 70%), the product nevertheless remained colourless after the bisque firing at 1350–1400°C. This fact confirms the necessity of the presence of lithium ions which, being the least bulky of alkali ions, can enter the zirconium silicate structure to a

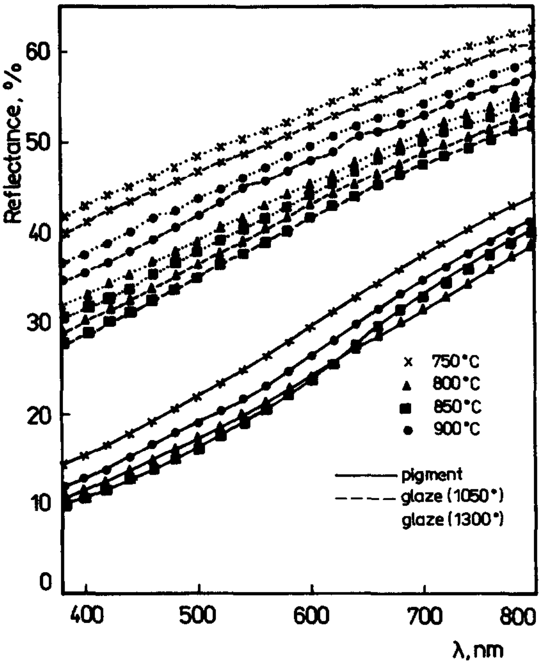

Fig. 6. The colour hue of these brown pigments (———) synthesised at temperatures: 750°C (×), 800°C (▲), 850°C (■) and 900°C (●) (for time 1·5 h) (after the bisque firing at 1400°C) and the colour hue of middle-temperature glaze (temperature of glazing 1050°C; – – –) and high-temperature glaze (1300°C; ······) with 10% (w/w) used pigments.

larger extent. Being negatively uncharged defects, they compensate the higher-valence ions, especially tellurium ions, in order to fulfil the condition of electroneutrality (the tellurium ions are *de facto* positively charged defects); this enables their entering and incorporation into the pigment structure. In the second case we replaced, in the mixture M_2, molybdenum trioxide by ammonium paratungstate. After 2 h calcination at 850°C (conversion degree above 80%), the colourless product was submitted to bisque firing at 1350–1400°C to give a pigment with a high intensity of brown colour. The result corresponded to the best pigments prepared from the mixtures containing MoO_3 (the M_2 mixture, the optimum conditions of calcination and bisque firing). The possibility of replacement of molybdenum ions by tungsten ions agrees with the above conclusion that the colouring defects in the zircon pigment predominantly are the higher-valent tellurium ions; without them it is impossible to prepare this pigment.

The optimum temperature conditions for the synthesis of this brown pigment were confirmed by the above-mentioned conversion degree of the calcinate into the pigment, and also by the colour hue of the pigments (after the bisque firing at 1400°C) as well as that of the ceramic glazes containing these pigments (Fig. 6). The most intense brown zircon pigment can be obtained from the M_2 mixture at synthesis temperatures of 800–850°C maintained for 1·5 h. Its application to a medium-temperature borate–silicate glaze (the glazing temperature of 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 of 1300°C). This confirms a good thermal stability of the pigment, which is quite sufficient for all purposes of ceramic glazing.

4 CONCLUSION

The brown zirconium silicate pigment is best prepared by the procedure suggested in this communication from the starting mixture (M_2) containing (% w/w): 47·76 ZrO_2, 23·88 SiO_2, 5·97 Na_2SiF_6, 4·48 $LiOH.H_2O$, 5·97 MoO_3 and 11·94 K_2TeO_4. Advantageous calcination temperatures and times are 800–850°C and 1–1·5 h, respectively. After extraction with diluted HCl, the colourless calcinate is submitted to a short (about 10 min) bisque firing at temperatures of 1350–1400°C to produce an intense brown pigment. The pigment exhibits high thermal and chemical stability and can be applied to all types of ceramic glazes, including high-temperature ones (with the glazing temperatures of 1300°C). When used in amounts of 3–10% (w/w) it effectively imparts a brown hue and these glazes are smooth, glossy and without any surface unevenness.

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