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Synthesis of a Yellow Zircon Pigment

M. Trojan

Institute of Chemical Technology, Lenin Sqr. 565, Pardubice, 532 10 Czechoslovakia

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SUMMARY

The thermal process has been adopted for the synthesis of the yellow pigment $Zr_{1-x}Pr_xSiO_4$ from the starting oxides ZrO_2 and SiO_2. The reactions of the synthesis have been followed by thermal analysis, analysis of the products prepared in the electric furnace under various conditions (temperature, time) and tableting (labelling) experiments. The two types of ZrO_2 used are those also currently utilized in the industrial production of the zircon pigments. Their reactivity has been evaluated and the synthesis conditions have been determined. The kinetics and mechanism of the reactions are also discussed.

INTRODUCTION

The yellow pigment $Zr_{1-x}Pr_xSiO_4$ represents a relatively new[1] means of coloration of ceramic glazes. It belongs to the modern group of zircon pigments[2,3] which exhibit high thermal, chemical and colour stabilities. There are only a few theoretical papers[4–6] dealing with the synthesis of the yellow pigment, none of them describing the application of thermal analysis (TA). This fact is connected with the problems of realization of the TA methods in the conditions of synthesis of the zircon pigments, as has already been mentioned in our previous report[7] on the blue pigment. The temperature and time dependencies of the formation of the yellow pigment during calcination have not yet been examined, due probably to difficulties connected with the determination of the conversion degree;[8] this problem was only solved quite recently.[9] Application of the so-called labelling experiments to investigation of the reactions and/or transport of the

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individual components in the mixture during synthesis of the yellow $Zr_{1-x}Pr_xSiO_4$ pigment has already been described,[4,10] but the experiments used in those studies evoke some doubt about the conclusions. We therefore modified them on the basis of our previous reports[7,11] and developed the so-called tableting variant.

EXPERIMENTAL

The synthesis of the yellow $Zr_{1-x}Pr_xSiO_4$ pigment is based on the reaction of the starting mixture of ZrO_2 and SiO_2 oxides in the presence of mineralizers (NaF and NaCl) and a chromophore (Pr_6O_{11}). The starting mixtures correspond in their composition to those used in the pigment production (mol%): 43·70 ZrO_2; 44·00 SiO_2; 5·86 NaF; 6·19 NaCl: 0·25 Pr_6O_{11}. (In TA and tableting experiments we also used the corresponding mixture without the chromophore: 43·81 ZrO_2; 44·11 SiO_2; 5·88 NaF; 6·20 NaCl.) The starting ZrO_2 samples were industrially used oxides, i.e. ZrO_2-7 of mineral origin (purified baddeleyite from the company Goldschmidt) and synthetic oxide CRO-1 (USSR). The granulometric composition and purity of the oxides are comparable,[12] but the Soviet oxide contains a higher content of phosphorus impurities (0·98%).[13] The other starting oxide used, SiO_2, was a single sample only,[13] since this oxide has no distinct effect on the course of the pigment synthesis proper.[12]

The experimental conditions used for following the synthesis of the yellow pigment are similar to those used in our recent paper[7] dealing with the blue zircon pigment and we shall therefore mention them only briefly here.

The TA analyses were carried out (Figs 1 and 2) with a Derivatograph Q-1500 apparatus (MOM Budapest; system of J. Paulik, F. Paulik and L. Erdey). Pure $ZrSiO_4$ proved to be a useful standard, air or argon being used as the atmosphere. The inner walls of the furnaces were protected with corundum coating against gaseous halogenides. The DTA sensitivity was 1/2, that of DTG was 1/2, and that of TG 20 and/or 50 mg. The heating was always finished after recording the exothermic peak of formation of the pigment. The peaks were evaluated (T_i, T_f, ΔH, E, n, I),[14–16] and the samples after TA were analysed for the conversion degree (α) and Pr content (x).

The arrangement of the tableting experiments is shown in Fig. 3. The transport of a certain component participating in the synthesis (pigment or pure $ZrSiO_4$) was determined, at a suitable combination of the components in the tablets, from the degree of yellow coloration of the adjacent faces of the tablets. In the absence of the chromophore we determined analytically[12] the amount of $ZrSiO_4$ formed on the adjacent faces of the tablets.

The temperature regions of formation of the $Zr_{1-x}Pr_xSiO_4$ pigment (in

isothermal conditions) and/or the kinetic curves were determined by following the conversion degree of the starting mixtures calcinated in the electric furnace at various temperatures (in the range 700–1100°C for 300 min; see Fig. 4) or at four chosen temperatures (800, 850, 900 and 1000°C) for various time intervals (Fig. 5). The kinetic curves were evaluated mathematically.[17]

RESULTS AND DISCUSSION

The thermoanalytic curves of the starting mixtures for preparation of the yellow $Zr_{1-x}Pr_xSiO_4$ pigment (heating rate 10°C min^{-1}; Fig. 1) have practically the same course up to 900°C for both the ZrO_2 samples used. Initially we can see a release of small amounts of moisture from components of the mixture up to 200°C. In the temperature range from 260 to 300°C a small endothermic effect was observed. This is caused by the reduction of the mixed oxide Pr_6O_{11} to Pr_2O_3, which is accompanied by a slight mass decrease (about 0·09%), precisely corresponding to the oxygen released [eqn (1)] (cf. TA of the starting mixture not containing the chromophore; Fig. 2):

$$Pr_6O_{11} = 3\,Pr_2O_3 + O_2 \qquad (1)$$

Thereafter, the sample mass remains practically unchanged up to 450°C, no energy changes being observed either. In the interval from 460 to 600°C a mild but perceptible mass decrease (about 0·1%) begins. This is connected with a slight endothermic arrest on the DTA curve, which is made more distinct at 575–580°C by a sharp endothermic peak (cf. Fig. 2). This is

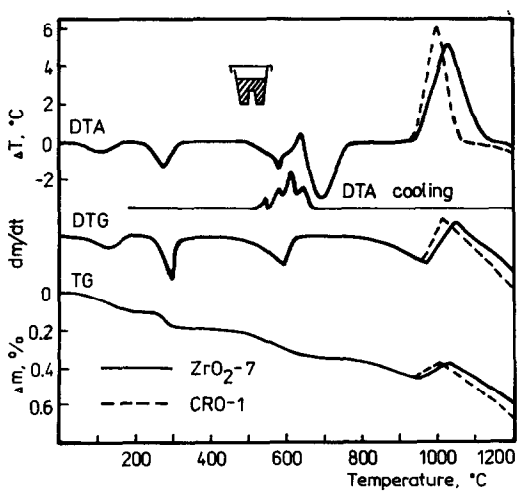

Fig. 1. Thermoanalytical curves of the starting mixtures for the synthesis of the yellow $Zr_{1-x}Pr_xSiO_4$ pigment with different ZrO_2 samples.

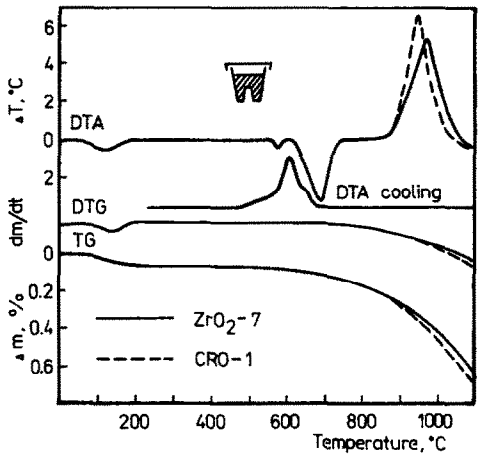

Fig. 2. Thermoanalytical curves of the starting mixtures for the synthesis of $ZrSiO_4$ with different ZrO_2 samples.

followed at temperatures above 600°C (when the sample mass attained a steady state again) by a mild exothermic effect with a sharp maximum at 630°C (cf. Fig. 2). The processes taking place in the interval from 460 to 635°C can be ascribed (in the first part up to 575°C) to a slow exothermic reaction [eqn (2)] between praseodymium(III) oxide and sodium chloride; in this way, very small amounts of greenish praseodymium(III) chloride are formed which escape from the mixture[5] (this fact was confirmed by the tableting experiments). (The reaction is supported by the presence of SiO_2 which shifts the equilibrium of eqn (2) slightly to the right, as was confirmed by independent TA of the mixtures Pr_2O_3–NaCl, Pr_2O_3–SiO_2 and Pr_2O_3–NaCl–SiO_2.)

$$Pr_2O_3 + 6\,NaCl + 3\,SiO_2 = 2\,PrCl_3 + 3\,Na_2SiO_3 \qquad (2)$$

Immediately after the endothermic modification transformation of quartz [eqn (3)] at 575–580°C this substance reacts (with operation of the Hedwall effect and participation of other components of the mixture) to give praseodymium disilicate [eqn (4)] in the interval from 590 to 640°C (the product identity was proved by X-ray diffraction analysis):

$$\alpha\text{-}SiO_{2(quartz)} = \beta\text{-}SiO_{2(quartz)} \qquad (3)$$

$$Pr_2O_3 + 2\,SiO_2 = Pr_2Si_2O_7 \qquad (4)$$

Then there follows a distinct endothermic process (peak width of 640–760°C, maximum at 690°C), i.e. formation of a melt of alkali components of the mixture. This corresponds to the temperature of melting of the NaF–NaCl eutectic[18] into which the other liquid and solid components formed by the reactions (1), (2) and (4) are transferred. Above 600°C the sample mass is

TABLE 1
Experimental Values (TA 10°C min^{-1}) Found for the $Zr_{1-x}Pr_xSiO_4$ Pigment (a) and Pure $ZrSiO_4$ (b) Formation from the Different ZrO_2 Samples

Starting ZrO_2	T_i (°C)	T_f (°C)	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	I	n	α	$x \times 100$	
								From TG	*Analytical*
ZrO_2-7 (a)	940	1130	−16·1	112·9	0·57	0·95	0·68	1·89	1·88
CRO-1 (a)	930	1060	−17·2	96·4	0·70	1·05	0·81	1·77	1·79
ZrO_2-7 (b)	880	1040	−18·2	80·1	1·00	0·77	0·92	—	—
CRO-1 (b)	880	1060	−18·4	83·0	1·26	1·10	0·89	—	—

almost unchanged at first, but, with increasing temperature, the melt phase attacks, more and more, the grains of the starting oxides, particularly SiO_2 [eqns (5) and (6)]:

$$(n+3)SiO_{2(s)} + 4\,NaX_{(l)} = SiX_{4(g)} + 2\,Na_2SiO_{3(l)} + n(SiO_2)_s \quad (X = F, Cl) \tag{5}$$

In this way the silicate component is transformed into a transportable form, i.e. gaseous tetrahalogenide, and the melt of alkali-silicate type. The partially released SiX_4 escapes from the mixture at this time (Δm is about 0·1% in the temperature range 800–930°C) because the pigment synthesis [eqn (6)] has not yet started at these conditions. The Pr^{3+} ions are, at these temperatures, obviously sufficiently fixed in the melt phase, hence the praseodymium chloride is not released any longer; therefore, the course of the TG curve, in this temperature region, is comparable with the TG curve of the starting mixture without the chromophore (Fig. 2), Δm at 800–900°C about 0·07%.

The exothermic reaction of the pigment synthesis at the heating rate of 10°C min^{-1} starts at 930 and 940°C in the cases of CRO-1 and ZrO_2-7 samples, respectively (Table 1).

From the tableting experiments (Fig. 3) it is possible to suggest (in accordance with ref. 4 and in contradiction to ref. 14) the reaction (6) for the synthesis proper of $ZrSiO_4$ as the pigment basis:

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

However, these experiments also showed that reaction (7) can also be significant, as has already been noted.[20] Our results indicate that its importance will be lower compared with the syntheses of other zircon pigments:[7]

$$(Na_2SiO_3)_{(l)} + ZrO_{2(s)} = ZrSiO_{4(s)} + (Na_2O)_{(l)} \tag{7}$$

Thus the ZrO_2 grains are attacked by mobile silicate components. They are also pre-corroded by the action of the alkali halogenide melt [eqn (8)], which also contributes to the pigment synthesis:

$$2\,ZrO_2 + 2\,NaCl = Na_2ZrO_3 + ZrOCl_2 \tag{8}$$

The formation of the zirconium(IV) compounds has been indicated previously.[5] However, the amount of these products is, according to our results, slight and prevents their transport to be proved on a macro scale in the tableting experiments. Important side-products are also formed by the reactions (6) and (7), in addition to the $ZrSiO_4$ microcrystals. First of these are the halogens (F_2, Cl_2), whose presence is essential for the formation of pigment. Due to their high electronegativity they can shield the strong mutual repulsive forces between silicon(IV) and zirconium(IV) ions,[21] and thus facilitate the mutual approach and reaction of these ions. The other side-product, the melt phase enriched in the Na_2O component, serves for the necessary regeneration of active oxygen in the mixture [eqn (9)]:[22]

$$Na_2O_{(l)} + X_2 = 2\,NaX_{(l)} + \tfrac{1}{2}O_2 \qquad (9)$$

The importance of a sufficient amount of oxygen (particularly in its active form) and of its continuous regeneration [the oxygen cycle: eqns (6) and (9)] was confirmed in our previous report.[7] Due to its high electronegativity, oxygen has similar favourable mineralization effects to the halogens mentioned above. In contrast to previous findings,[7] however, the oxygen cycle in the present case is not affected positively, but negatively, by the chromophore. The synthesis of the yellow $Zr_{1-x}Pr_xSiO_4$ pigment is shifted by 50–60°C to higher temperatures compared with that of the synthesis of pure $ZrSiO_4$ (without the chromophore; Fig. 2). The praseodymium present in its trivalent state in the melt phase of the mixture must be transformed into the tetravalent state at the moment of formation of the pigment. Only in this way can it be incorporated into the zircon structure of the pigment in the form of substitution uncharged defects in the place of zirconium (Pr^{x}_{Zr}); these defects are responsible for the required yellow hue of the pigment. However, in this way oxygen is exhausted from the mixture [eqns (10) and (11)]:

$$SiX_4 + (1-x)ZrO_2 + \frac{x}{2}Pr_2O_3 + \left(1+\frac{x}{4}\right)O_2 = Zr_{1-x}Pr_xSiO_4 + 2X_2 \qquad (10)$$

$$(Na_2SiO_3) + (1-x)ZrO_2 + \frac{x}{2}Pr_2O_3 + \frac{x}{4}O_2 = Zr_{1-x}Pr_xSiO_4 + Na_2O \qquad (11)$$

This conclusion is reliably documented by the breaks in the TG curves at the moment of the pigment synthesis, when the slow steady mass decrease of the sample stops. The mass is even perceptibly slowly increased, which is connected with the incorporation of gaseous oxygen into the solid phase of the pigment formed, due to the transition of praseodymium into the tetravalent state [(10) and (11)]. The values of these mass increases (after extrapolation to the TG curve course for the synthesis of pure $ZrSiO_4$; Fig. 2) are about 0·074% and 0·070% for the starting CRO-1 and ZrO_2-7 samples,

TABLE 2

Temperatures[a] of $Zr_{1-x}Pr_xSiO_4$ Pigment Synthesis for Two Sources of ZrO_2 Measured by TA under an Atmosphere of Air or Ar at Various Heating Rates (2·5–20°C min^{-1})

	Atmosphere									
	Ar		*Air*							
	Heating rate (°C min^{-1})		*Heating rate* (°C min^{-1})							
	10		*2·5*		*5*		*10*		*20*	
	T_i	T_f	T_i	T_f	T_i	T_f	T_i	T_f	T_i	T_f
ZrO_2-7	960	1 150	850	910	885	1 010	940	1 130	970	1 160
CRO-1	945	1 100	870	940	895	1 020	930	1 090	950	1 100

[a] T_i and T_f measured in °C.

respectively. The values of praseodymium content of the $Zr_{1-x}Pr_xSiO_4$ pigment calculated from these mass changes related to the conversion degree found (α; Table 1) and hypothetical equation (12) are in good accordance with the analysis of TA products (Table 1). Negative consequences of insufficient amounts of oxygen during the pigment synthesis were confirmed by TA carried out in an inert atmosphere (Table 2). The reaction of the pigment synthesis is shifted to higher temperatures, the shift being greater with ZrO_2-7. The CRO-1 oxide has a much larger specific surface;[11] hence, even after passing argon through it, its micropores retain sufficient amounts of oxygen up to the reaction temperatures. Independent experiments of the pigment synthesis in an electric furnace under argon confirmed the above findings, especially in the case of the mixtures with ZrO_2-7 when the resulting product hue was only slightly yellowish, even if the conversion degree of the mixture was sufficient. For the synthesis of pure $ZrSiO_4$ (without the chromophore) the effect of an inert atmosphere appeared to be indistinct for both the oxides. Hence, unless the above-mentioned oxygen circulation [eqns (6) and (9)] is markedly disturbed in some way (e.g. by the effect of the chromophore), it is practically self-sufficient. Another source of upset of the oxygen circulation is the presence of impurities in the starting materials. In our previous communication[7] we have already pointed out the unfavourable effects of the phosphorus impurity present in the Soviet ZrO_2 sample on the synthesis of the blue $Zr_{1-x}V_xSiO_4$ pigment, and which are caused by its undesirable reaction with the chromophore. In the case of the synthesis of the yellow $Zr_{1-x}Pr_xSiO_4$ pigment, however, this impurity has favourable effects, phosphorus being transformed from its pentavalent form to tetravalent.[12] The reason is that it is easily trapped in the structure of the pigment formed, in the form of a substitution uncharged defect, particularly in the place of zirconium (P^x_{Zr}).[23] Due to its small ionic radius, it can also be

trapped in the place of silicon (P_{Si}^{x}). This process is accompanied by transformation of P^{V} to P^{IV} with release of the necessary active oxygen, and which can be represented by eqn (12):

$$(1-x)ZrO_2 + (1-y)SiO_2 + \frac{(x+y)}{2}P_2O_5 = Zr_{1-x}P_{(x+y)}Si_{1-y}O_4 + \frac{(x+y)}{4}O_2 \quad (12)$$

The oxygen cycle is thus suitably complemented, and this is one of the reasons why the synthesis of the yellow $Zr_{1-x}Pr_xSiO_4$ pigment is better accomplished (reaction temperatures and rates, yields, hue of products) with the CRO-1 oxide than with ZrO_2-7. However, the amount of phosphorus in the Soviet oxide and, hence, the amount trapped in the pigment is small and the possibility of introduction of praseodymium ions into the pigment structure is therefore only slightly lowered (Table 1), so the yellow hue of the pigment is not impaired. The presence of phosphorus imparts a slightly reddish, 'warmer' hue to the yellow pigment, which is often advantageous. This result was confirmed by addition of 1% phosphorus (in the form of ZrP_2O_7) to the starting mixture with ZrO_2-7; the conversion degree was increased by about 5% and the colour hue became comparable with that of the pigment produced from the Soviet oxide.[11]

The course of the exothermic reactions of the pigment synthesis recorded on the DTA curves at a basic heating rate of $10°C\,min^{-1}$ showed that the Soviet oxide CRO-1 was more reactive under these conditions (cf. the ΔH and E values in Table 1). In addition to the above favourable effect of the phosphorus impurity, the reason also lies in the higher specific surface of this oxide.[11] Its micropores can more easily retain the oxygen necessary for the reaction (6) as well as the halogens released in the reaction. However, the most significant reason lies in the existence of two basic mechanisms of transfer of the silicate component and, hence, of the pigment synthesis reactions (6) and (10), and (7) and (11). As was shown by the tableting experiments (Fig. 3) and the analyses of the calcinates prepared under isothermal conditions in the electric furnace (Figs 4 and 5), each of these mechanisms is dominant in a certain temperature region. At the given TA conditions, the pigment synthesis shifts to the temperature region, where the governing process consists in the transfer (and reaction) of the silicate component in the tetrahalogenide gas phase [eqns (6) and (10)]. The Soviet oxide, having a greater specific surface, better fulfils the prerequisites of the reactions under these conditions. The TA showed (Table 2) that the ZrO_2-7 oxide becomes more reactive than CRO-1 at lower heating rates and the pigment synthesis commences at lower temperatures, where the dominant mechanism consists in the transfer of silicate component by the melt phase. This phase (at the conditions of slower heating) can favourably influence the

ZrO_2 grains for a longer period [eqn (8)]. The ZrO_2-7 oxide is of mineral origin and has relatively well-developed crystal surfaces. The crystals, however, contain a relatively large amount of impurities in their monoclinic structure[13] in the form of defects, resulting in an enhanced number of vacancies which are markedly mobile with increasing temperature. This especially supports the participation of this oxide in the reactions with the melt phase [eqns (13)–(15)]:

$$4\,NaX + nZrO_2 = 4\,X_O^{\cdot} + v_{Zr}^{''''} + (n-1)ZrO_2 + 2\,Na_2O \qquad (13)$$

$$4\,X_O^{\cdot} + v_{Zr}^{''''} + ZrO_2 + Na_2O = 2\,Na_{Zr}^{'''} + 3\,O_O^{x} + Zr_{Zr}^{x} + 3v_O^{\cdot\cdot} + X_2 \qquad (14)$$

$$2\,Na_{Zr}^{'''} + 3\,O_O^{x} + Zr_{Zr}^{x} + 3v_O^{\cdot\cdot} + SiO_2 = ZrSiO_4 + Na_2O \qquad (15)$$

($4\,X_O^{\cdot}$ denotes four substitution positively charged defects, formed by halogen in the position of oxygen anion, and $3v_O^{\cdot\cdot}$ denotes three positively charged defects, formed by vacancies in the oxygen lattice. The existence of $Na_{Zr}^{'''}$ and $X_O^{\cdot}$ defects in the zircon pigment has been confirmed in a previous study.[12])

The DTA curves of cooling (Fig. 1) exhibit three smaller endothermic effects and one more distinct one. The first is in the region of 670–640°C, the second more distinct one is in the region 640–585°C, the third, again smaller, at 580–550°C, and the fourth at 550–530°C. The third effect is obviously connected with a small modification transformation of the remaining SiO_2-quartz (β-modification $\rightarrow$ α-modification) in the mixture; the other three effects are due to gradual solidification of the components of the melt phase in the calcinate.

The tableting experiments confirmed the conclusion that each of the two basic mechanisms of the synthesis of the $Zr_{1-x}Pr_xSiO_4$ [eqns (10) and (11)] has the dominant role in the individual temperature regions. Figure 3 shows that transitions between the two mechanisms take place at 950 and 980°C in the case of the CRO-1 and ZrO_2-7 oxides, respectively. This result agrees well with the TA results; at smaller heating rates (2·5 and 5°C min^{-1}), when the main parts of the exothermic effects lie above these temperatures, the ZrO_2-7 is more reactive than CRO-1 and vice versa. The tableting experiments also showed an interesting observation concerning the transfer of the praseodymium-containing component. At lower temperatures this is transported by the liquid melt phase (in accordance with ref. 4), whereas at higher temperatures it also can be transported by the gas phase. However, this cannot occur until at the moment of the pigment synthesis, and even then to a very low extent. The TA results have excluded any sample mass decreases due to vaporization of some praseodymium compound to the area outside the reaction mixture (cf. the TG curves in Figs 1 and 2).

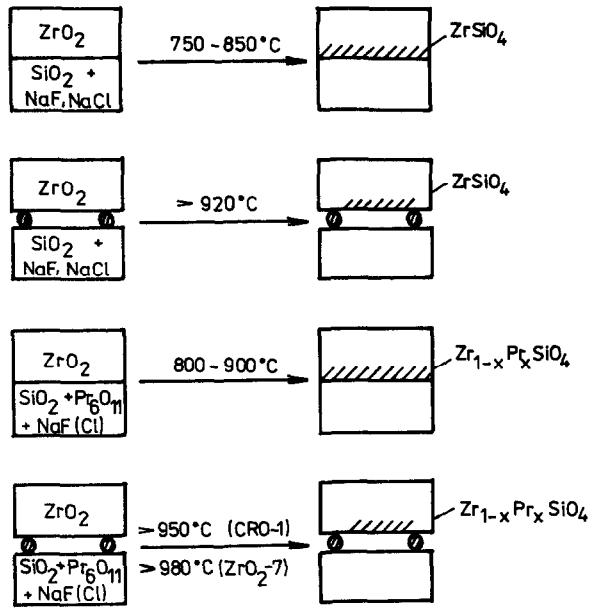

Fig. 3. Tableting experiments (○, platinum ring).

The existence of two basic mechanisms of the pigment synthesis and their validity in individual temperature regions was confirmed unambiguously by the conversion degrees of the pigments prepared under isothermal conditions in an electric furnace. The curves in Fig. 4 show clear breaks which can only be explained by a change in the dominant mechanism of the reactions of the pigment synthesis at these temperatures. This change takes place at 950°C with the CRO-1 oxide, whereas with ZrO_2-7 it lies higher by about 30–50°C. Hence suitable temperatures for the pigment synthesis appear to be in the interval from 850 to 900°C or about 1000°C and above.

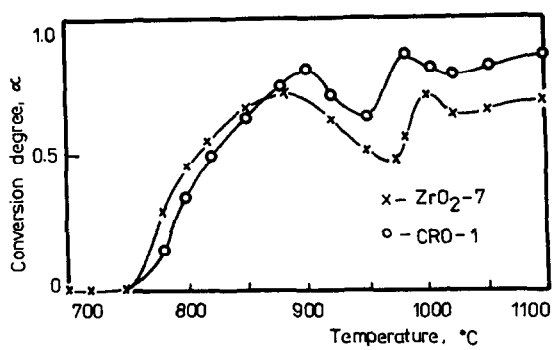

Fig. 4. Conversion degree of different ZrO_2 samples to yellow $Zr_{1-x}Pr_xSiO_4$ pigment at various calcination temperatures (time 300 min).

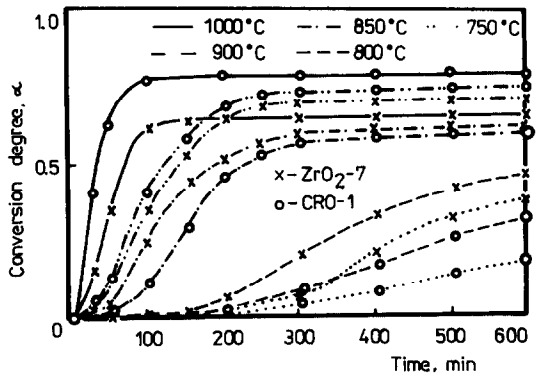

Fig. 5. Kinetic curves for synthesis of yellow $Zr_{1-x}Pr_xSiO_4$ pigment at various calcination times (temperature 750, 800, 850, 900 and 1000°C).

The different reactivity of the starting ZrO_2 oxides and the existence of various mechanisms were also confirmed by examination of the kinetics of the pigment synthesis (Fig. 5) and its mathematical evaluation (Table 3). At temperatures below 850°C the reaction is faster and the conversion degree is higher for ZrO_2-7 than for CRO-1, whereas above 900°C the opposite is true. At temperatures of 750 and 800°C the kinetic curves are best described by equations of such models which involve random nucleation of ZrO_2 grains (eqn F1 in ref. 14) and/or also the processes at the phase interface (eqns R2 and R3 in ref. 14) as the rate-limiting steps. At 850 and 900°C the predominant processes are those at the phase interface (R2 and R3) between the melt phase and ZrO_2 grains. At 1000°C (and 900°C) the process consists in volume diffusion of one component (gaseous SiX_4) through the layer of the $Zr_{1-x}Pr_xSiO_4$ product, i.e. the equation devised by Žuravlev–Lesochin–Tempelman (ZLT), Ginstling–Brounštejn and Kröger–Ziegler.[14] The necessary calcination times were 3–4 h and 1·5–2 h for the suggested suitable temperatures for the pigment syntheses, i.e. 850–900°C and about 1000°C, respectively.

TABLE 3

Rate Constants of the Kinetic Models Satisfying the Synthesis Course of $Zr_{1-x}Pr_xSiO_4$ Pigment from the Different ZrO_2 Samples at Various Temperatures

Starting ZrO_2	*Average values of rate constants* ($s^{-1} \times 10^{-7}$)				
	Temperature (°C)				
	750	*800*	*850*	*900*	*1000*
ZrO_2-7	$k_{F1} = 48$	$k_{R3} = 50$	$k_{R2} = 166$	$k_{ZLT} = 112$	$k_{ZLT} = 113$
CRO-1	$k_{F1} = 44$	$k_{R3} = 54$	$k_{R2} = 156$	$k_{ZLT} = 136$	$k_{ZLT} = 342$

CONCLUSION

The reaction of formation of the yellow zircon pigment $Zr_{1-x}Pr_xSiO_4$ represents a mildly exothermic process ($-\Delta H \simeq 16$–$17\,kJ\,mol^{-1}$). Several mechanisms can operate in the pigment synthesis. With increasing temperature (at about 750°C) the rate-limiting process consists in random nucleation of the ZrO_2 grains by the melt of the alkali-silicate type formed in the reaction mixture. At about 850°C the governing step changes to the processes at the phase interface between the melted silicate phase and ZrO_2 grains. Above 900°C (i.e. the temperatures used in practice for the pigment synthesis) the volume diffusion is rate-limiting, the silicate component being transferred. Above 950–980°C the predominant diffusion is that of the SiX_4 to unreacted ZrO_2 grains or to the inner parts of these grains through the layer of the product already formed ($Zr_{1-x}Pr_xSiO_4$ pigment). The chromophore component (Pr) is also mobile through the liquid phase and, at higher temperatures, also to a small extent through the gas phase. Praseodymium is oxidised to the tetravalent state at the moment of the pigment synthesis, which consumes oxygen in the mixture and decreases the mineralization effects in the reaction mixture.

At lower temperatures (up to 850°C) the ZrO_2-7 oxide of mineral origin is more reactive under the conditions of the synthesis of the $Zr_{1-x}Pr_xSiO_4$ pigment, because its favourable structure with a large number of defects (and vacancies) enables its easier participation in the reactions based on random nucleation or interfacial processes. At higher temperatures the CRO-1 oxide (synthetic) appears to be more reactive. Its insufficiently developed microcrystals with strongly furrowed surfaces are suitable for the processes based on volume diffusion, which is decisive at higher temperatures. In addition, at higher temperatures the phosphorus impurity present in this oxide also has a favourable effect.

REFERENCES

1. K. Fuji and K. Sono, *Rep. Gov. Res. Inst. Ceram., Kyoto*, **6**, 18 (1952).
2. F. T. Booth and G. N. Peel, *Trans. Brit. Ceram. Soc.*, **61**, 359 (1962).
3. A. Broll, H. Beyer and P. Kleinschmit, *Chem.-Ztg*, **101**, 319 (1977).
4. R. A. Eppler, *Ind. Eng. Chem., Prod. Res. Dev.*, **10**, 352 (1971).
5. J. Kvapil, J. Hnízdil, E. Příhoda and M. Koloc, *Silikáty*, **22**, 139 (1978).
6. M. Trojan and Z. Šolc, *Proc. ZIRCONIA '86 Tokyo II*, Tokyo, Uchida Rokakuho Publishing Co. 335 (1987).
7. M. Trojan, *Dyes and Pigments*, **9**, 221 (1988).
8. M. Trojan, *Chem. Listy*, **80**, 640 (1986).
9. M. Trojan, Czech. Patent 233691 (1984).

10. R. A. Eppler, *Amer. Ceram. Soc. Bull.*, **56**, 213 (1977).
11. M. Trojan, *Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice*, **45**, 287 (1982).
12. M. Trojan and Z. Šolc, *Silikáty*, **28**, 222 (1984).
13. M. Trojan, *Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice*, **44**, 255 (1981).
14. A. Blažek, *Termická analýza*, Prague, SNTL (1972).
15. H. E. Kissinger, *J. Res. Nat. Bur. Std*, **57**, 217 (1956).
16. G. O. Pilojan, *Vvedenije v teoriju termičeskovo analiza*, Moscow, Izd. Akad. Nauk (1964).
17. J. M. Sharp and J. O. Hancock, *J. Amer. Ceram. Soc.*, **55**, 74 (1972).
18. D. Penfold and A. Hellawell, *J. Amer. Ceram. Soc.*, **48**, 133 (1965).
19. A. S. Bystrikov, *Steklo Keram.*, **22**, 5 (1965).
20. T. Hibino, T. Y. Yamazaku and H. Sekyia, *Kogyo Kagaku Zasshi*, **69**, 2068 (1966).
21. M. Trojan, Z. Šolc and M. Kuchler, *Silikáty*, **29**, 125 (1985).
22. M. Trojan and Z. Šolc, *Proc. Conf. TERMANAL '82, High Tatras, 1982*, p. 233.
23. M. Trojan, *Chem. Listy*, in press.
24. Z. Šolc, M. Trojan and H. Prokopová, *Chem. Prům.*, **35/60**, 121 (1985).