Dyes and Pigments **9** (1988) 329–342

Synthesis of a Pink Zircon Pigment

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(Received 8 July 1987; accepted 18 August 1987)

ABSTRACT

A pink zircon pigment of the inclusion type, $(ZrSiO_4)_{1-x} \cdot xFe_2O_3$, has been synthesized by a thermal process from the starting oxides ZrO_2 and SiO_2. Green vitriol (ferrous sulphate) or ferric oxide–hydroxide have been used as the chromophore (source of the inclusions). The reactions in the synthesis have been followed by thermal analysis, by analysis of the products prepared under isothermal conditions at various temperatures and during various reaction times in an electric furnace, and by tableting (marking) experiments. Two types of commercial ZrO_2 have been used, both of them being raw materials for industrial production of zircon pigments. Reactivity of these oxides has been evaluated, the conditions of the pigments synthesis have been determined and the reaction mechanism and kinetics have been investigated.

INTRODUCTION

The pink zircon pigment is the newest representative[1] of the pigments based on zirconium(IV) silicate and with a zircon structure.[2,3] These pigments exhibit high thermal and chemical stabilities and fastness of colour hue and are used for the colouration of ceramic glazes. The available reports pertaining to the pink zircon pigment are predominantly patents, and only a few investigations[4-6] have been concerned with theoretical aspects. Moreover, conclusions of these reports are contradictory. The discrepancies concern the structure of this pigment and/or its colouring action, and also the explanation of the mechanism of the reaction of formation of this pigment. Most workers[4-6] accept the hypothesis expressed in the marketing

Dyes and Pigments 0143-7208/88/$03·50

prospectus.[7] This publication suggests that the structure of the pink pigment is the same as those of the two other well-known zircon pigments, i.e. the blue $Zr_{1-x}V_xSiO_4$[8,9] and the yellow $Zr_{1-x}Pr_xSiO_4$.[10,11] Hence, the pigment is represented[7] by the formula $Zr_{1-x}Fe_xSiO_4$, and its red (pink) hue is ascribed to the ions of tetravalent iron (or to an equimolecular mixture of hexavalent and bivalent iron). It was not until another study[6] that it was confirmed (in accordance with our own investigation[12,13] that the pink zircon pigment is of the so-called inclusion type. It is formed by microcrystals of zirconium(IV) silicate with the zircon structure with mechanically incorporated particles of red α-Fe_2O_3 (haematite) which impart the final pink hue to the product. From this fact we derive the formula of the pigment in the form $(ZrSiO_4)_{1-x}.xFe_2O_3$ which is used in the present communication.

No reports can be found in the literature concerning the evaluation and description of the reactions involved in the synthesis of the pink zircon pigment using thermal analysis (TA). This fact is connected with the problems of realization of the TA methods in the conditions of synthesis of zircon pigments as has been mentioned in our previous report[9] on the blue zircon pigment. No reports are available on a quantitative investigation of the synthesis of the pink pigment and its dependence on the calcination temperature and time, the only exceptions being the data found in ref. 14. This, in turn, is probably due to the difficulty in determining the conversion degree in the production of zircon pigments,[15] a problem which has only recently been surmounted.[16] The application of the so-called marking experiments to investigations of the reactions and/or transport of the individual components in the mixture during synthesis of the pink pigment has already been described in the literature,[4] but the arrangement of the experiments used evoked some doubts about the validity of the conclusions. We have now modified these experiments, on the basis of our previous studies,[9,11] into the so-called tablet variant.

EXPERIMENTAL

The synthesis of the pink $(ZrSiO_4)_{1-x}.xFe_2O_3$ pigment is based on a reaction of the oxides ZrO_2 and SiO_2 with the mineralizer (NaF and NaCl) in the presence of a chromophore ($FeSO_4.7H_2O$ or $FeO.OH$). In addition, the starting mixtures also contained KNO_3 as an oxidant. The starting mixtures (A, B) correspond in their composition (Table 1) to those used practically in the pigment production. The ZrO_2 used was either a commercial product, namely ZrO_2-7 of mineral origin (purified baddeleyite from the company Goldschmidt) or a synthetic material CRO-1 of Soviet

TABLE 1

Composition of the Starting Mixtures (A, B) used for the Synthesis of the Pink Pigment

Component	*Composition of the mixture (mol%; mass%)*	
	A	*B*
ZrO_2	29·78; 39·70	30·78; 48·23
SiO_2	32·00; 20·80	31·27; 23·82
NaF	20·80; 9·45	20·93; 11·17
NaCl	7·46; 4·72	7·30; 5·43
KNO_3	2·42; 2·65	2·36; 3·04
$FeSO_4.7H_2O$	7·54; 22·68	— —
FeO.OH	— —	7·36; 8·31

origin. Both the granulometric composition and chemical purity are comparable for these two samples,[17] the only difference being a higher content of phosphorus impurities (0·98%) in the latter.[8] The second basic component was a commercial SiO_2 of mineral origin; this oxide has no distinct effect on the course of the pigment synthesis proper.[8]

The experimental conditions used for the investigation of the synthesis of the pink pigment are similar to those used in our recent paper[9] dealing with the analogous synthesis of a blue zircon pigment. As they are fully described there, only brief details are given here.

The Derivatograph Q-1500 apparatus (MOM Budapest, system of J. Paulik, F. Paulik, L. Erdey) was used for the TA (Fig. 1); pure $ZrSiO_4$ was used as standard and an atmosphere of air was employed. The inside walls of furnaces were protected from gaseous halogenides by means of corundum coating. Sensitivity: DTA 1/5, DTG 1/5, and TG 200 mg (above 600°C, DTA, DTG 1/2, TG 50 mg). The heating was stopped in all cases at 1000°C. The exothermic effects of the pigment formation were evaluated (T_i, T_f, ΔH, E, n, I),[18-20] and the samples after TA were analysed for the conversion degree α and the Fe_2O_3 content x.

With regard to the relatively high proportion of mineralizer and chromophore and/or oxidant in the starting mixture, it was possible to expect distinct changes in the mass of the calcinated mixture A as a consequence of vaporization of some intermediates. Therefore, we also followed the mass changes of the calcinates during calcination under isothermal conditions in an electric furnace within the temperature range 700–900°C (Fig. 2). We also presumed a high residue of extractable components in these calcinates. Therefore, the calcinates were submitted to a two-step extraction after cooling. The first extraction used distilled water (10 min, boiling) and the second extraction used hydrochloric acid of

20 mol % concentration (also 10 min boiling). After each extraction, the solid phase was separated by filtration, dried and weighed, and the extractable portions of the calcinate were thus calculated (Fig. 2). These results also contributed to the evaluation of the mechanism of the pink zircon pigment synthesis.

The arrangement of the tableting experiments is represented in Fig. 3. The transport of a certain component participating in the synthesis reaction (pigment or pure $ZrSiO_4$) was determined, at suitable combinations of components in the tablets, on the basis of the pink colouration of the adjacent faces of the tablets. In the experiments without chromophore, the $ZrSiO_4$ formed on the adjacent tablet faces was analysed.[16]

The temperature regions of formation of the $(ZrSiO_4)_{1-x}.xFe_2O_3$ pigment (under isothermal conditions) and 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 from 650 to 950°C for 300 min; Fig. 4) and at two chosen temperatures (800 and 850°C for ZrO_2-7 and CRO-1, respectively) for various time intervals (Fig. 5), respectively. The kinetic curves were evaluated mathematically.[21]

RESULTS AND DISCUSSION

The thermoanalytic curves (heating rate $10°C\,min^{-1}$; Fig. 1) of the starting mixtures A and B for the preparation of the pink pigment $(ZrSiO_4)_{1-x}.xFe_2O_3$ exhibit practically the same course in both cases up to 730°C.

In the case of the mixtures with the $FeSO_4.7H_2O$ chromophore (the mixtures and TA curves denoted with A), there occurs initially a marked endothermic process (peak width 65–230°C) connected with liberation of the predominant part of the water of crystallization from the green vitriol. This dehydration is followed by a less endothermic process, accompanied by a small mass decrease at about 320°C (decomposition of an intermediate small amount of hydroxide–sulphate).[23] However, compared with the decomposition of green vitriol itself,[22] the dehydration process of the thermoanalysed mixture is not complete until 450°C. At this point there appears another small endothermic process, accompanied by a mass decrease. This process cannot be ascribed to anything other than the completion of the dehydration. Decomposition of KNO_3 is indistinct until above 550°C (which was confirmed by TA). Independent TA of various combinations of two, three and four components (out of $FeSO_4.7H_2O$, NaCl, NaF, SiO_2, ZrO_2) confirmed that the above-mentioned is predominantly due to a reaction between green vitriol and sodium chloride (sodium fluoride does

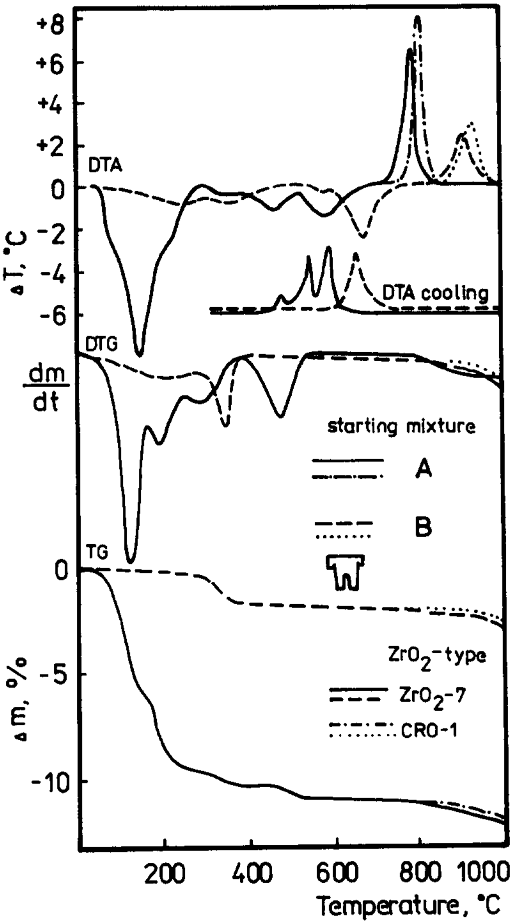

Fig. 1. Thermoanalytical curves of the starting mixtures (A, B) for the synthesis of the pink $(ZrSiO_4)_{1-x}.xFe_2O_3$ pigment with different ZrO_2 samples.

not react in this way). At the beginning of the dehydration of the green vitriol, the compound dissolves in its own water of crystallization and sodium chloride is transferred partially into this liquid phase. This dissolution is accompanied by partial formation of an intermediate sodium–ferrous hydroxide–sulphate, which shifts the final dehydration up to the above-mentioned temperature.[23] In the temperature range 530–650°C the DTA curve further shows a distinct endothermic effect, without any mass change. This corresponds to formation of a melt into which alkali and also, partially, ferrous cations and halogenide, sulphate and nitrate anions are transferred. Ferrous ions form, with the help of the melt, an intermediate of the ferrous halide type (the diffraction lines of FeF_2 were confirmed in a corresponding, independently calcinated mixture) which is partially oxidized to the trivalent state due to the oxidic character of the melt. The overall mass decreases in

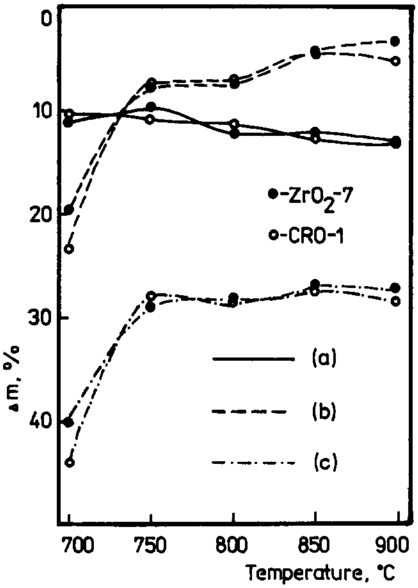

Fig. 2. Percentage weight losses caused by the calcination of the starting mixture A (two different ZrO_2 used) (a); and percentage weight extracted from these calcinates with boiling water in one step (b) or in two steps with water and 20% hydrochloric acid (c).

the TG curves are above 10% even with the isothermally calcinated mixtures (Fig. 2) at about 700°C, which corresponds very precisely to total dehydration of green vitriol in the mixture (theoretically 10·2%). Also in the next temperature region (up to 1000°C) the mass decrease is only slow. This means that no decomposition of the sulphate component takes place in the calcinated mixture, as was the case with pure ferrous sulphate.[22] The reason lies in formation of sodium sulphate, the existence of which was confirmed by X-ray diffraction analysis in cooled samples of independently calcinated mixtures ($FeSO_4.7H_2O$, NaF, NaCl, and ZrO_2 or SiO_2). In this way the sulphate ions are fixed in the calcinated mixture and do not undergo decomposition. With increasing calcination temperature the alkali-halide melt phase attacks more and more the grains of the starting SiO_2 [eqn (1)].

$$(n+3)SiO_{2(s)} + 4NaX_{(l)} = SiX_{4(g)} + 2Na_2SiO_{3(l)} + nSiO_{3(s)} \quad (X = F, Cl) \tag{1}$$

This is supported also by the modification transformation of quartz, which makes the endothermic effect more distinct in this region of temperature [eqn (9)]. Thus the silicate component is transformed into a transportable state, i.e. into gaseous tetrahalide and a melt of alkali silicate type. The SiX_4, thus partially released, escapes from the mixture, since the pigment synthesis [eqn (4)] has not yet started at these temperatures. The transient ferrous halide also reacts with silicon oxide to give SiX_4 [eqn (2)]. Partial vaporization of the halides mentioned (those of silicon and iron) then causes a continuous slight mass decrease of the sample thermoanalysed (*ca* 35% in the interval 500–730°C).

$$2FeX_2 + SiO_2 + \tfrac{1}{2}O_2 = SiX_4 + Fe_2O_3 \qquad (2)$$

Again, α-Fe_2O_3 was confirmed by X-ray diffraction analysis in the mixtures independently calcinated at the corresponding temperatures. Its formation affects decisively the final hue of the pigment.

In order to attain the conditions necessary for the pigment synthesis, alkali sulphate must exert its special function, i.e. it attacks, partially, the grains of the other starting oxide, ZrO_2, in the melt phase to give the oxide–sulphate, eqn (3), (the formation of which was confirmed by X-ray diffraction analysis of independently calcinated samples).

$$ZrO_2 + Na_2SO_4 = ZrOSO_4 + Na_2O_{(l)} \qquad (3)$$

This explains the relatively large extractable portion from the calcinates prepared at a temperature of 700°C. This portion exceeds the mass of the other components remaining in the mixture, i.e. the soluble residue of mineralizer, chromophore, and the portion of SiO_2 which has not yet been converted to the pigment (cf. Figs 3 and 4). Hence, the extractable form must also include a part of the ZrO_2 which has also not yet reacted in the pigment formation.

The exothermic reaction of the pigment synthesis in the TA conditions starts at 730 and 760°C with the oxides ZrO_2-7 and CRO-1, respectively. (The values determined from the exothermic effect recorded are given in Table 2.) The tableting experiments (Fig. 3) confirmed that reaction (4) can be suggested for the synthesis proper of $ZrSiO_4$, as the pigment basis, in accordance with ref. 4 and in contrast with ref. 24.

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

A simultaneous reaction produces α-Fe_2O_3 [eqn (2)] whose particles are immediately incorporated into the microcrystals of the $ZrSiO_4$ thus formed to give the pink pigment $(ZrSiO_4)_{1-x}.xFe_2O_3$. The same reaction releases SiX_4 which is immediately involved in the reaction of formation of the

TABLE 2

Experimental Values (TA 10°C min^{-1}) Found for the Pink $(ZrSiO_4)_{1-x}.xFe_2O_3$ Pigment Formation from the Individual ZrO_2 Samples (Starting Mixture A)

Starting ZrO_2	T_i (°C)	T_f (°C)	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	I	n
ZrO_2-7	730	830	−19·3	68	1·14	1·43
CRO-1	760	840	−18·1	72	1·00	1·26

silicate [eqn (4)], which favourably shifts the equilibrium of the reaction (2). The tableting experiments confirmed that the reaction (5) is also significant in the pigment synthesis; and this has also been pointed out by other workers.[25]

$$(Na_2SiO_3)_{(l)} + ZrO_{2(s)} = ZrSiO_{4(s)} + (Na_2O)_{(l)} \qquad (5)$$

The ZrO_2 grains are also already preliminarily damaged by the action of the aggressive melt phase as well as by partial formation of zirconium(IV) oxide–sulphate [eqn (3)]. This compound reacts readily with the melt phase of the alkali silicate to give the required product [eqn (6)].

$$ZrOSO_{4(l)} + Na_2SiO_{3(l)} = ZrSiO_4 + Na_2SO_4 \qquad (6)$$

The tableting experiments (Fig. 3) confirmed this reaction by recording a partial transport of the zirconium (IV) component through the liquid phase. Thereby the importance of the transport of the components through the liquid phase is increased and so also is the corresponding mechanism of the reactions of the pink pigment synthesis [eqns (5) and (6)]. This is in contrast to the synthesis of the yellow zircon pigment investigated in our earlier work[11] in which a mechanism with the transfer of silicate component through a gaseous phase predominated.

The reactions in eqns (3), (4) and (5) also produce important side-products. First of these are halides (F_2, Cl_2) whose presence is inevitable for the pigment formation. Due to their high electronegativity they can shield the mutual repulsive forces between silicon(IV) and zirconium(IV) ions,[26] and thus facilitate their mutual approach and reaction. The other side-product, the melt phase enriched in Na_2O, can act as a source of the necessary regeneration of active oxygen in the mixture [eqn (7)].[27]

$$Na_2O_{(l)} + X_2 = 2NaX_{(l)} + \tfrac{1}{2}O_2 \qquad (7)$$

The importance of a sufficient amount of oxygen (especially in its active form) and its continuous regeneration [the oxygen cycle—eqns (3), (4) and (5)] was confirmed in our previous communications.[9,11] In contrast with the syntheses of the blue and yellow zircon pigments,[8,11] its importance is not so great for the pink pigment. The oxygen consumption in the reaction of eqn (2) is sufficiently satisfied by the oxidic character of the melt phase (the presence of oxidic anions of sulphur and nitrogen). Hence, the course of TG curves at the moment of the pigment synthesis also shows no mass changes (increases) which could be due to binding of gaseous oxygen by the Fe component into the solid phase of the reaction mixture (as was the case with the yellow zircon pigment.[11] Above the temperatures corresponding to completion of the pigment synthesis (Table 2), however, the TG curves show a certain break, and the mass decrease increases more distinctly with increasing temperature. This can be explained by the increased volatilization of the remaining silicon halides (or iron halides) which cannot be bound by the reactions (3) and (2), respectively.

A somewhat simpler reaction course is seen from the TA of mixture B (with FeO.OH as chromophore) (Fig. 1). At first, about 300°C, ferric oxide–hydroxide is transformed into the oxide in an endothermic process connected with a mass decrease [eqn (8)]. At 575–580°C a well-perceptible endothermic effect of the modification transformation [eqn (9)] can be seen, and at 670°C the eutectic mixture NaF–NaCl melts.[28]

$$2\mathrm{FeO.OH} = \mathrm{Fe_2O_3} + \mathrm{H_2O} \tag{8}$$

$$\alpha\text{-}\mathrm{SiO}_{2(\mathrm{quartz})} = \beta\text{-}\mathrm{SiO}_{2(\mathrm{quartz})} \tag{9}$$

The exothermic effects of formation of the pink pigment appear at temperatures more than 100°C higher than those with the mixture A, and they are smaller. (The reaction temperatures then roughly approach those of formation of pure $ZrSiO_4$ determined in our previous work;[11] obviously, the difference is due to the presence of KNO_3 and the higher content of NaF.) The results, however, show that the application of green vitriol as the chromophore in the synthesis of the pink pigment is very important. This chromophore increases the mineralization effects of alkali halides (lowering of the temperature of synthesis; increase in its exothermicity) and enables a more intensive colouration of the pigment to be attained. This latter effect is due to the fact that the colouring haematite inclusions are predominantly formed only at the moment of the pigment synthesis and, hence, are more effectively incorporated into the zirconium silicate microcrystals. If ferric oxide–hydroxide is applied, then (as was shown by TA) haematite is already formed at about 300°C, a temperature which is far lower than that of the pigment synthesis, hence trapping of its inclusions is less efficient. This result was also confirmed by analysis of TA samples (Table 3) which determined both the conversion degree of the pigment and the haematite content in the

TABLE 3

Analysis of the Pink Pigment $(ZrSiO_4)_{1-x}.xFe_2O_3$ Prepared Under the Conditions of TA

Quantity measured	*Starting mixture and oxide*			
	A($FeSO_4.7H_2O$)		*B(FeO.OH)*	
	ZrO_2-7	*CRO-1*	*ZrO_2-7*	*CRO-1*
Conversion degree (α)	0·86	0·83	0·75	0·71
Haematite content (x)	0·065	0·060	0·016	0·014

pigment. As is seen from Table 3, the conversion degree of the pigment is 10–15% higher with green vitriol than with ferric oxide–hydroxide and the content of colouring inclusions is even greater (roughly four times). On the basis of these results it is possible to express the composition of the pink zircon pigment (with green vitriol as the chromophore) by the formulas $(ZrSiO_4)_{0{\cdot}935}.0{\cdot}065Fe_2O_3$ and $(ZrSiO_4)_{0{\cdot}94}.0{\cdot}06Fe_2O_3$ for the starting ZrO_2-7 and CRO-1, respectively.

These results show that the ZrO_2-7 oxide is more reactive and leads to a better product under the conditions of the synthesis of the zircon pigment. This oxide is of mineral origin and its crystals have relatively well-developed surfaces. They contain, however, a relatively large number of impurities in its monolithic structure[10,17] and which are present in the form of defects. Therewith closely connected is the existence of an increased number of vacancies which are distinctly mobile with increasing temperature.[29] They support involvement of this oxide particularly in the reactions with the melt phase [eqns (10)–(12)].

$$4NaX + nZrO_2 = 4X_O^{\bullet} + v_{Zr}^{''''} + (n-1)ZrO_2 + 2Na_2O \qquad (10)$$

$$4X_O^{\bullet} + v_{Zr}^{''''} + ZrO_2 + Na_2O = 2Na_{Zr}^{'''} + 3O_O^{x} + Zr_{Zr}^{x} + 3v_O^{\bullet\bullet} + X_2 \qquad (11)$$

$$2Na_{Zr}^{'''} + 3O_O^{x} + Zr_{Zr}^{x} + 3v_O^{\bullet\bullet} + SiO_2 = ZrSiO_4 + Na_2O \qquad (12)$$

The importance of the melt for the pink pigment synthesis (the starting mixture A) with regard to its composition and volume, makes itself very evident even up to high calcination temperatures. In this case, this lowers the importance of the gas phase (as already mentioned), which otherwise is decisive for the other zircon pigments[9,11] at high temperatures.

For the cooling process the TA method showed that the mass of the samples changes no further. However, the DTA curves (Fig. 1) exhibit exothermic effects of solidification of the melt phase. In the case of mixture B, the single exothermic effect found corresponds very well to solidification of the eutectic NaF–NaCl. The A mixture, however, exhibits three exothermic effects in the region of 530–580°C. Hence, the melt components solidify separately. With respect to the multicomponent character of the melt and its variable composition (due to the completed pigment synthesis and partial vaporization of some components), however, it would be difficult to specify the individual solidification effects in more detail.

For the tableting experiments (Fig. 3) FeO.OH was used as the chromophore, since the application of green vitriol caused melting of the tablets. However, sulphate ions were added to the mixture in the form of Na_2SO_4 to make the conditions similar to those with application of green vitriol. The experiments showed that the two mechanisms [eqn (4) and eqns (5)–(6)] of the synthesis of the $(ZrSiO_4)_{1-x}.xFe_2O_3$ pigment have their

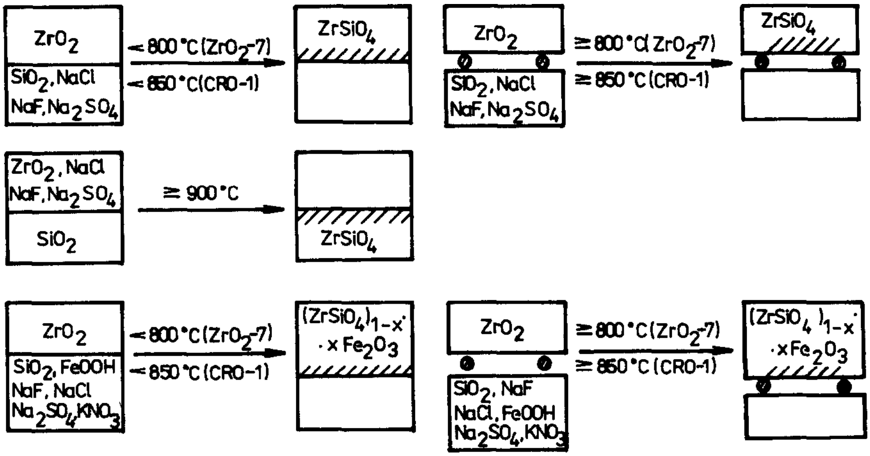

Fig. 3. Tableting experiments (●, platinum ring).

distinct importance in the low-temperature regions. The temperatures of 800 and 850°C (for the starting oxides ZrO_2-7 and CRO-1, respectively) can be considered as boundaries between the validity intervals of these mechanisms. Below these temperatures the transfer and reaction, of the silicate component in the liquid melt phase [eqn (5)] is predominant and at higher temperatures processes in the gas phase are also significant. Compared to previous studies[9,11] dealing with other zircon pigments, the transition between the two mechanisms is not so marked. It can be presumed that both exist equally within a broad temperature region. This is also supported by the partial transition of the zirconium(IV) component into the mobile melt phase, which was recorded by the tableting experiments at higher temperatures (at least 900°C). Also recorded was the transportability of a chromophore component (in contrast to ref. 4) through the liquid phase and, at higher temperatures, even the gas phase.

The existence of two basic mechanisms of the pigment synthesis and their somewhat increased validity in different temperature regions was then unambiguously confirmed by the conversion degree of the pigments in isothermal conditions in an electric furnace. The curves in Fig. 4 show different, but well-perceptible breaks, which can only be explained by a change in the governing mechanism of the pigment synthesis reactions at these temperatures. The temperatures of these changes are 800 and 850°C for the starting oxides ZrO_2-7 and CRO-1, respectively. Hence, suitable temperatures for the pigment synthesis appear to lie either at 750 and 800°C for the oxides ZrO_2-7 and CRO-1, respectively, or at 900°C and above this temperature for both the oxides. Different reactivities of the starting ZrO_2 was also confirmed by kinetic measurement of the pigment synthesis reactions (Fig. 5) at 800°C (ZrO_2-7) and 850°C (CRO-1). It was

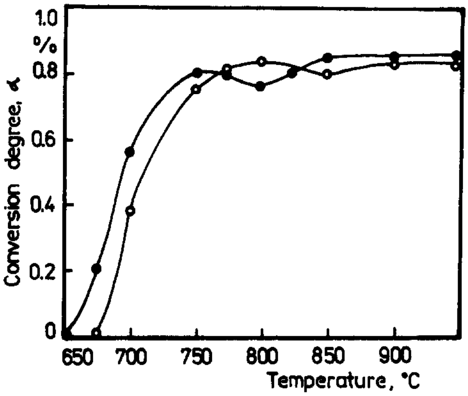

Fig. 4. Conversion degree of different ZrO_2 samples (starting mixture A) to pink $(ZrSiO_4)_{1-x} \cdot xFe_2O_3$ pigment at various calcination temperatures (time 300 min).

found that, for the CRO-1 oxide under these conditions, the conversion degree reaches its maximum value (0·83) as early as after 1 h calcination; the corresponding values for ZrO_2-7 were 0·87 and 2 h. Mathematical treatment of the curves showed that their course is closest to the equations of the models[21] of Ginstling–Brounštejn and Žuravlev–Lesochin–Tempelman (ZLT, Table 4). Hence, under these temperature conditions, the process consists in volume diffusion (of gaseous SiX_4) through the layer of the $(ZrSiO_4)_{1-x} \cdot xFe_2O_3$ product to the ZrO_2 grains that have not yet reacted. However, the kinetic curves also agree relatively well with the equations of models involving the rate-limiting processes at the phase interface (R2, R3, Table 4). This phase interface is between the melt phase of the alkali-silicate type (as well as zirconium(IV) oxide–sulphate) and the solid phase of ZrO_2 grains. Thereby it is confirmed that in the pink pigment synthesis in this case

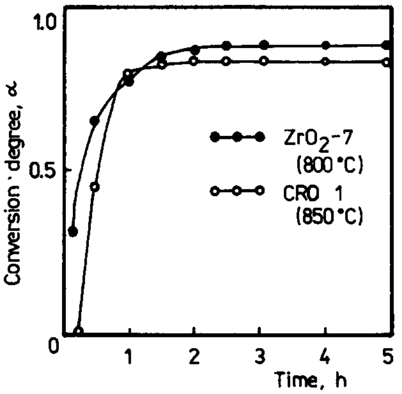

Fig. 5. Kinetic curves for the synthesis of the pink $(ZrSiO_4)_{1-x} \cdot xFe_2O_3$ pigment.

TABLE 4

Rate Constants of the Kinetic Models Satisfying the Synthesis Course of $(ZrSiO_4)_{1-x}.xFe_2O_3$ Pigment from the Various ZrO_2 Samples at 800 and 850°C

Starting *ZrO_2*	*Temperature* (°C)	*Average values of rate constants* ($s^{-1} \times 10^{-7}$)		
ZrO_2-7	800	$k_{ZLT} = 963$	$k_{R3} = 811$	$k_{R2} = 1\,007$
CRO-1	850	$k_{ZLT} = 751$	$k_{R3} = 636$	$k_{R3} = 811$

the predominance of one of the two basic mechanisms over the other is not so marked.

CONCLUSION

The reaction of formation of the pink zircon pigment $(ZrSiO_4)_{1-x}.xFe_2O_3$ is a mildly exothermic process ($-\Delta H \simeq$ 18–19 kJ mol^{-1}). Two mechanisms play decisive parts in the pigment synthesis. Below 800°C (ZrO_2-7) or 850°C (CRO-1) the rate-limiting process is the transfer and reaction of the silicate component in the form of a liquid melt of the alkali-silicate type. At higher temperatures, the transfer and reaction of this component in the form of SiX_4 slightly predominate. However, the transition between the two mechanisms is not as distinct as with other zircon pigments.[9,11] This is due to the higher content of the melt phase in the reaction mixture, as well as to a more distinct participation of the chromophore in some reactions preceding the pigment synthesis. In this respect the sulphate ions from the chromophore are particularly favourable. They increase the proportion of the melt phase and enable the transition of the silicate component to the form of mobile and reactive zirconium(IV) oxide–sulphate. They also support the transition of the ferrous component from the chromophore to the form of the colouring inclusions of the haematite type. The ferrous component, in its turn, contributes to 'attraction' of the starting SiO_2 into the reaction of formation of SiX_4. It was also shown that the ferrous component can be the mobile component in the reaction mixture predominantly in the liquid melt phase (at lower temperatures) or even in the gas phase (at higher temperatures).

The oxide ZrO_2-7 appears to be more reactive in the whole temperature range investigated and this is due to its mineral origin and high content of defects (vacancies) in its structure. These defects enable its easier involvement in the pigment synthesis reactions based predominantly on participation of the melt phase.

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