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Synthesis of a Blue Zircon Pigment

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SUMMARY

Thermal analysis (DTA, DTG, TG), calcination of the starting mixture in an electric furnace at various temperatures and for different periods of time, and tabletting (marking) experiments have been used to evaluate the reactions involved in the synthesis of the blue zircon pigment $Zr_{1-x}V_xSiO_4$. *Three industrial samples of* ZrO_2 *were evaluated as the starting zircon components. The temperature of the pigment synthesis was determined for each of three samples, their different reactivity explained, and the mechanism and kinetics of the pigment formation investigated.*

INTRODUCTION

The zircon pigments are typical of modern high-temperature pigments used in ceramics[1,2] and the blue pigment $\mathrm{Zr_{1-x}V_xSiO_4}$[3–5] is one of the most important representatives. Only studies dealing with the application of thermal analysis (TA) to a study of their preparation have been previously described.[6,7] Other than our previous reports,[8–10] no other data have been reported which deal with the exothermic effects of the pigment formation. One of the main difficulties in such investigations is related to the volatility of the halogenides, the occurrence of which in the area of the oven of the thermoanalyser can result[4] in damage to the equipment. Additionally, difficulties arise in the estimation of the conditions of the TA and in the necessity of changing the DTA and TG sensitivity during the TA, this being the only way by which reliable recording can be made of the effects of the

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mildly exothermic reaction of the pigment formation together with the slight mass changes of the sample at the moment of reaction. We have found the TA method to provide a quick and reliable procedure. No data on the conversion degree of the blue pigment at various temperatures and on the reaction kinetics of its formation have been reported. This is connected with the difficult determination of the conversion degree of the pigment,[11] a problem only recently overcome using the method developed in our laboratories.[12] The so-called marking experiments had been used previously[13] to trace the transport of the silicate component in the calcinated mixture during the synthesis of zircon pigments. These experiments, however, involved a direct contact of loose mixture components, which prevented an unambiguous differentiation between the transport through the gas phase and that due to capillary elevation of the liquid phase. This problem was successfully overcome, by pressing the starting mixture components into tablets which, in addition, could be separated by a platinum ring.[9]

This present communication is concerned with the most frequently produced and used zircon pigment—blue $Zr_{1-x}V_xSiO_4$ (with colouring admixture of V^x_{Zr} = vanadium in the position of zirconium as an uncharged defect (x)).[3-5] Its synthesis is based on the reaction of the basic starting oxides—ZrO_2 and SiO_2—with addition of the mineralizers (NaF and NaCl) and of the chromophore (NH_4VO_3). The starting mixtures correspond in their composition to those used in pigment production (mol%): 37·84 ZrO_2, 38·73 SiO_2, 6·34 NaF, 13·67 NaCl, 3·42 NH_4VO_3. The zircon(IV) raw material used was based on three different industrial oxides, namely ZrO_2-7 (Goldschmidt) of mineral origin, and two synthetic oxides—CRO-1 (USSR) and ZrO_2-S (MEL). Granulometric composition and chemical purity of the oxides are comparable,[4,5] only the Soviet oxide containing a higher amount of a phosphorus impurity (0·98% P). As the second basic component for the reaction mixture an industrial oxide SiO_2 was used (only one type was used since this oxide has no significant influence on the course of the synthesis).[5]

The starting mixtures were thermoanalysed under non-isothermal conditions (Fig. 1) with a Derivatograph Q-1500 apparatus (MOM Budapest, system of J. Paulik, F. Paulik, L. Erdey). For the standard we used $ZrSiO_4$ synthesised in the same way as the pigments and purified. The thermal properties of this are similar to those of the pigment and it proved to be better than the usual standard α-Al_2O_3. Both the sample and the standard were provided with a corundum cover during the TA to protect the inside of the oven from the volatile halogenides. The TA sensitivity was selected lower (DTA 1/10, TG 200 mg) in its initial stage (up to 500–600°C) where the reactions between the mineralizer components or chromophore occur with marked energy and mass changes. The sensitivity was then increased (DTA

1/2, TG 20 mg) and this enabled trapping of the mild energy or mass change connected with the reaction of the pigment formation. After recording the whole exothermic effect, heating was stopped, and the sample was analysed for the $ZrSiO_4$ content.[12] From the DTA curves were then calculated[14–16] the reaction enthalpy values, the formal activation energies, and thence the temperatures of the beginning and end of the reaction (T_i, T_f), the reaction order (n), and the symmetry index I of the peak.

The tabletting (marking) experiments employed in this study also, in a way, represent a TA method. The tablets, with various suitably combined individual components of the starting mixture (Fig. 2), were placed on each other either with or without direct contact (i.e. separated by a ring of Pt wire). Blue colouration of an adjacent face of some tablet (due to the pigment formation) indicates transportability of the given component participating in the reaction (with possible differentiation between the transport through the gaseous phase and that through the liquid phase). If the chromophore was not used then the zirconium(IV) silicate formed on the tablet surface was determined analytically.[12]

Additionally, the starting mixtures of the individual ZrO_2 samples were calcinated at isothermal conditions in an electric furnace, either for a constant time period of 300 min at various temperatures in a broad range of 600–1300°C or for different time periods at several chosen temperatures. The conversion degrees of the calcinate into the pigment were determined for various temperature dependences (Fig. 3) and kinetic curves (Fig. 4) of the pigment formation. The latter were evaluated mathematically by examination of the validity of the kinetic equations corresponding to various kinetic models.[17]

RESULTS AND DISCUSSION

The thermoanalytical curves (heating rate 10°C min^{-1}; Fig. 1) of the starting mixtures for the preparation of the blue $Zr_{1-x}V_xSiO_4$ pigment have practically the same course up to 700°C for all the three ZrO_2 samples studied. Above 150°C, NH_4VO_3 is converted into V_2O_5 with liberation of ammonia and water. This transformation is composed of three subsequent processes, in contrast to a previous report.[18] The first step can be described by eqn (1) in accord with earlier conclusions.[19] Trivanadate is formed with a distinct endothermic effect (peak width 150–200°C). (The mass decrease corresponds very accurately to two-thirds of the ammonia and water content in NH_4VO_3.)

$$3NH_4VO_3 = NH_4V_3O_8 + 2NH_3 + H_2O \qquad (1)$$

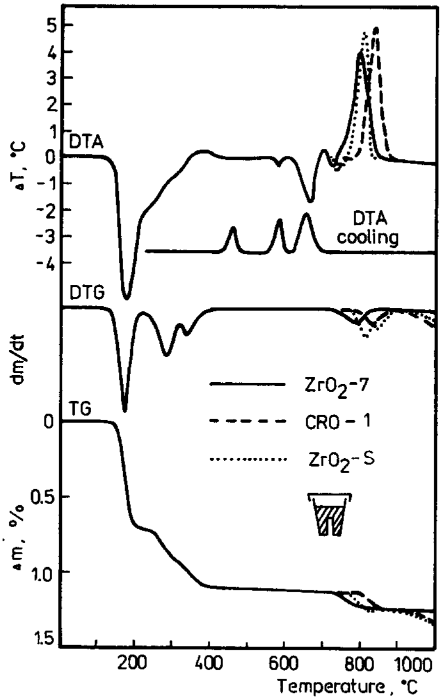

Fig. 1. Thermoanalytical curves of the starting mixtures for the synthesis of $Zr_{1-x}V_xSiO_4$ pigment with various ZrO_2 samples.

This intermediate is then transformed in the second (milder) endothermic process (peak width 250–320°C) into another intermediate [eqn (2)], also in agreement with previously reported conclusions.[20] (The mass decrease is precisely equal to one-half of the remaining ammonia and water in the intermediate.)

$$4NH_4V_3O_8 = (NH_4)_2V_{12}O_{31} + 2NH_3 + H_2O \qquad (2)$$

Thereafter, the third process begins, which already is slightly exothermic and is connected with the release of the remaining ammonia and water (peak width 330–400°C)

$$(NH_4)_2V_{12}O_{31} = 6V_2O_5 + 2NH_3 + H_2O \qquad (3)$$

The exothermicity of this process is obviously due to the fact that the otherwise endothermic character of the reaction (3) is overshadowed by crystallization of the originally formed amorphous V_2O_5 (this is a frequent phenomenon with the condensation reactions based on thermal dehydration[21]).

From 400 to 700°C the sample mass changes only slightly. The DTA curve exhibits a small but distinct endothermic effect of the modification transformation of quartz at 575°C [eqn (4)].

$$\alpha\text{-}SiO_{2(quartz)} = \beta\text{-}SiO_{2(quartz)} \tag{4}$$

At 600°C, the mixture of mineralizer and vanadium oxide begins to melt, and this is connected with a marked endothermic effect at 650–670°C. (This observation agrees well with the melting of the NaF–NaCl eutectic[22] and of V_2O_5.[19,23]) In this way, a melt of the type of sodium vanadate bronzes is formed;[24] its vanadate component partially releases oxygen [eqn (5)].[6,19]

$$V_2O_5 = V_2O_4 + \tfrac{1}{2}O_2 \tag{5}$$

With increasing temperature, this melt further attacks the grains of the starting oxides, especially SiO_2 [eqn (6)].

$$(n+3)SiO_{2(s)} + 4NaX_{(l)} = SiX_{4(g)} + 2(Na_2SiO_3)_{(l)} + n(SiO_2)_{(s)} \tag{6}$$

$$(X = F, Cl)$$

In this way, the silicate component is transformed into a transportable state—gaseous SiX_4 and a liquid (melt) of the type of alkali silicate and/or silicate-vanadate. The partial release of the gaseous tetrahalide (which, at these temperatures, escapes from the reaction mixture) is clearly seen in the mild but constantly growing mass decrease at the TG curve of the starting mixture without the chromophore (Fig. 1).

The vanadate component of the alkali melt, in addition, attacks the zirconium(IV) oxide and is transformed, to a slight extent, into divanadate [eqn (7)] in a mildly exothermic process about 700°C.[24]

$$ZrO_2 + 2V_2O_5 = ZrV_2O_7 \tag{7}$$

This intermediate, however, melts and decomposes at temperatures of 750–800°C,[25] immediately preceding the exothermic process of pigment formation. The considerable importance to this process from the point of view of the pigment synthesis proper has been described[26] in a less rigorous way, by eqns (8) and (9).

$$ZrO_2 + nV_2O_5 = ZrO_2\,.\,nV_2O_y + n(5-y)O \tag{8}$$

$$ZrO_2\,.\,nV_2O_y + SiO_2 = ZrSiO_4 + nV_2O_y \tag{9}$$

Transformation of a small part of ZrO_2 into a reactive and, at the same time, transportable form is thus indicated. This conclusion however contradicts earlier studies[13] but was confirmed by the tabletting experiments (Fig. 2). If the ZrO_2 of USSR origin is used (Fig. 1), then the above-mentioned formation and decomposition of the vanadate–zirconium(IV) intermediate is more complex. This is presumably due to the reaction of the vanadium

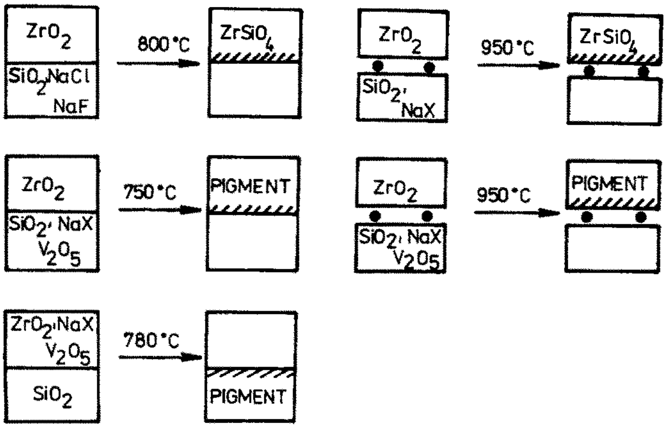

Fig. 2. Tabletting experiments (▨, platinum ring).

component of the melt with the phosphorus compound contained in this oxide as an impurity. Thus another intermediate is formed (at a temperature of 690–700°C), the presence of which could be confirmed but not identified by X-ray analysis. At higher temperatures, it is decomposed (at non-isothermal TA conditions this decomposition is not complete until 790°C). In spite of the fact that this intermediate only exists in a narrow temperature interval, its effect on the pigment formation reaction is unfavourable: with CRO-1 this reaction is shifted to higher temperatures. This can also be concluded from the exothermic effects found in the DTA curves (see Table 1), as well as from the temperature dependence of the pigment conversion degree (Fig. 3). At the lowest temperature the reaction proceeds with ZrO_2-7, the ZrO_2-S sample being in the middle, and CRO-1 reacts at the highest temperatures.

As already confirmed by the tabletting experiments (Fig. 2), eqn (10) can be

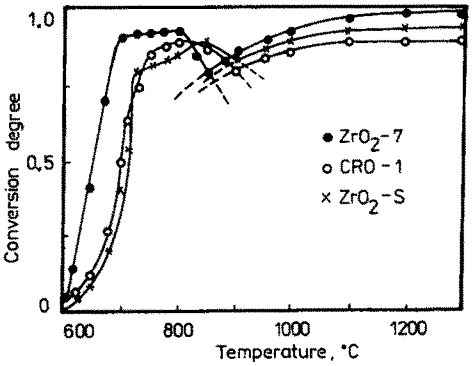

Fig. 3. The conversion degree of individual ZrO_2 samples to blue $Zr_{1-x}V_xSiO_4$ pigment at various calcination temperatures (time 300 min).

TABLE 1

Experimental Values found for $Zr_{1-x}V_xSiO_4$ Pigment 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
ZrO_2-7	730	840	−20·1	60	1·34	1·46	0·92	0·023
CRO-1	790	870	−18·5	89	0·82	1·14	0·87	0·025
ZrO_2-S	765	835	−16·9	72	0·80	1·13	0·89	0·030

suggested for the synthesis proper of zirconium(IV) silicate as the pigment basis.

$$SiX_{4(g)} + ZrO_{2(s)} + O_2 = ZrSiO_{4(s)} + 2X_{2(g)} \tag{10}$$

These experiments, however, confirmed that another reaction is also significant; this reaction, which has already been mentioned previously,[25] can be expressed schematically by eqn (11).

$$(Na_2SiO_3)_{(l)} + ZrO_{2(s)} = ZrSiO_{4(s)} + (Na_2O)_{(l)} \tag{11}$$

Thus the silicate component, in the form of transportable compounds (SiX_4, the alkali silicate melt) approaches the ZrO_2 grains, which have already been eroded [by the action of the aggressive melt of the sodium vanadate bronzes and by reactions (7) to (9)]. In addition to the $ZrSiO_4$ microcrystals, several other important side-products are also formed by reactions (10) and (11). Firstly, the halogens (F_2, Cl_2), the formation of which is necessary for the pigment formation: because of their high electronegativity they diminish the strong mutual repulsive forces between the silicium(IV) and zirconium(IV) ions[27] thereby enabling their approach and reaction. The other side-product, the melt phase enriched in the Na_2O component, affords the necessary generation of active oxygen in the mixture [eqn (12)].[28]

$$Na_2O_{(l)} + X_2 = 2NaX_{(l)} + \tfrac{1}{2}O_2 \tag{12}$$

Besides the slow release of oxygen from V_2O_5 which begins from about 400°C,[6] the TG curves (at high TG sensitivity) show small but distinct breaks at the point of the pigment formation (in contrast to the TG curves of the mixture without the chromophore). This indicates that the vanadium portion, trapped in the structure of the $ZrSiO_4$ microcrystals formed, is not transformed to the tetravalent state until the moment of pigment synthesis. The samples after TA were therefore extracted[12] to separate the pure pigments, which were then submitted to alkaline decomposition[29] and analysed for vanadium content (Table 2). The values obtained agreed very well with the vanadium content calculated from eqn (6) and from the breaks in the TG curves (Table 2).

TABLE 2
Vanadium Content (Expressed as x in the Formula $Zr_{1-x}V_xSiO_4$) in the Blue Pigments after TA

$Zr_{1-x}V_xSiO_4$ *pigment*	*x determined analytically*	*x calculated from TG*
From ZrO_2-7	0·023	0·024
From CRO-1	0·025	0·027
From ZrO_2-S	0·030	0·032

The reaction proper of formation of the blue zirconium pigment can thus be expressed by eqns (13) and (14).

$$SiX_4 + (1-x)ZrO_2 + x/2V_2O_5 + (1-x/4)O_2 = Zr_{1-x}V_xSiO_4 + 2X_2 \quad (13)$$

$$(Na_2SiO_3) + (1-x)ZrO_2 + x/2V_2O_5 = Zr_{1-x}V_xSiO_4 + Na_2O + x/4O_2 \quad (14)$$

The oxygen released from V_2O_5 is also favourable from the mineralization point of view (formation of $ZrSiO_4$ from the mixture without the chromophore). It complements the above-mentioned important oxygen cycle [eqns (10) and (12)] and, moreover since its electronegativity lies between those of fluorine and chlorine, it has a similar favourable effect in shielding the mutual repulsive forces between the silicium(IV) and zirconium(IV) ions.

The DTA curves of cooling indicate three exothermic effects (690–625°C, 600–565°C and 470–440°C). These effects are solidification of the melt occurring in three separate processes (modification changes cannot be assumed).

The tabletting experiments (Fig. 2) showed that each of the two basic mechanisms of the pigment synthesis (13) and (14) predominates in particular temperature regions. Up to 750–850°C (depending on the ZrO_2 type) the predominant reaction is (14), which involves the transfer of the silicon component through the liquid melt phase, whereas above this temperature the transfer is realized by the gaseous tetrahalide (13). A similar situation is encountered in the transport of the vanadium-containing component; at lower temperatures, the transport is predominantly realized by the melt phase of sodium vanadate bronzes, whereas at higher temperatures it is transferred into the gaseous phase. Hence, it is only at higher temperatures that our results agree with previous conclusions[29] regarding the transition of vanadium into gaseous oxide–fluoride [eqn (15)].

$$24NaF + 10V_2O_5 = 6V_2O_2F_4 + 8Na_3VO_4 + 3O_2 \quad (15)$$

$$V_2O_2F_4 + SiO_2 = V_2O_4 + SiF_4 \quad (16)$$

We have previously shown[4] that the first, lower-temperature mechanism is more favourable for incorporation of V^{4+} ions into the pigment structure: a greater portion of vanadium is trapped and the pigment has a more intensive blue hue. However, the conclusion[29] that SiX_4 [eqn (16)] is not further involved in the pigment formation proper is not substantiated by the results of our tabletting experiments.

The existence of two basic mechanisms for synthesis of the blue $Zr_{1-x}V_xSiO_4$ pigment and their validity for particular temperature regions was unambiguously confirmed by calcination of the starting mixture in an electric furnace at isothermal conditions (Fig. 3). The curves show a distinct break which can only be explained by a change in the reaction mechanism of the pigment synthesis occurring at these temperatures. The temperatures of this change are lowest for ZrO_2-7 (850°C) and are approx. 50°C higher for ZrO_2-S and CRO-1.

The higher reactivity of ZrO_2-7, as demonstrated in the TA, can be explained by its mineral origin; although it forms crystals with well-developed surfaces, it contains a large amount of impurities.[4] These impurities are present in the form of defects which are closely connected with the existence of an enhanced number of vacancies. The motions of these vacancies during heating facilitate the oxide taking part in reactions (13) and (14) of the pigment synthesis and reactions (6) and (7) with the chromophore. This was confirmed by the thermoelectrometric investigation[30] of the conductivity of the oxides. In the case of ZrO_2-7 (in contrast with the other two oxides) this conductivity is not markedly increased with increasing temperature. The CRO-1 and ZrO_2-S oxides appear to be prepared synthetically. Although they belong to the monoclinic system, their particles do not exhibit marked microcrystal character and they are formed by aggregates of irregular shape and surface. The ZrO_2-S sample contains less impurities and CRO-1 also contains a greater amount of the phosphorus impurities which detrimentally affect the reactivity of the oxide (see above).

Different reactivities of the individual ZrO_2 samples were also confirmed by kinetic measurements of the pigment formation (Fig. 4). Mathematical

TABLE 3

The Rate Constants of the Kinetic Models Suitable for Various Temperatures of the Pigment Synthesis from the Individual ZrO_2 Samples

Starting ZrO_2	*Average values of the rate constants ($s^{-1} \times 10^{-7}$) for various temperatures*					
	670°C	*690°C*	*710°C*	*730°C*	*760°C*	*800°C*
ZrO_2-7	$k_{F1} = 219$	$k_{R3} = 217$	$k_{ZLT} = 620$	$k_{ZLT} = 1\,412$	$k_{ZLT} = 3\,314$	$k_{D3} = 1\,430$
CRO-1	—	—	$k_{F1} = 405$	$k_{R3} = 198$	$k_{ZLT} = 887$	$k_{ZLT} = 3\,593$
ZrO_2-S	—	$k_{F1} = 143$	$k_{R3} = 156$	$k_{ZLT} = 461$	$k_{ZLT} = 1\,001$	$k_{ZLT} = 1\,663$

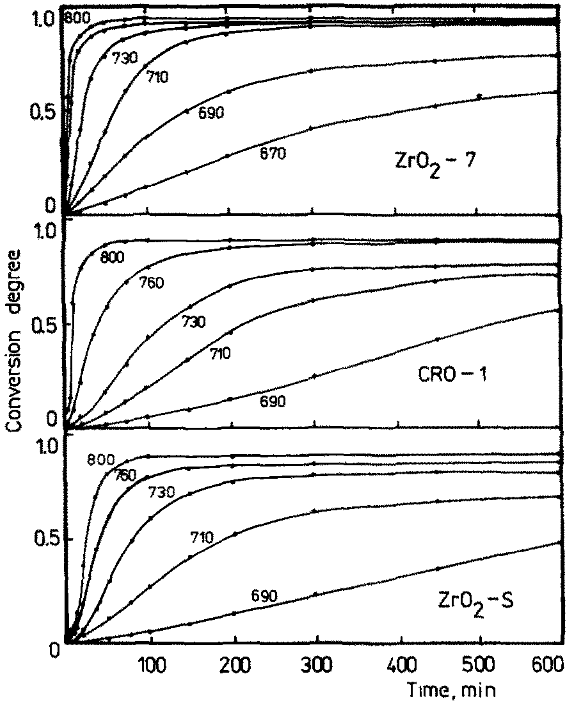

Fig. 4. Kinetic curves for the synthesis of the blue $Zr_{1-x}V_xSiO_4$ pigment at various calcination times (temperature 670, 690, 710, 730, 760, 800°C).

treatment of the kinetic curves (Table 3) supports the existence of the various mechanisms operating in the synthesis.[14,31] At the lowest temperatures (670, 690 and 710°C for the ZrO_2-7, ZrO_2-S and CRO-1 samples, respectively) it was found that even the kinetic models based on random nucleation were suitable [eqn (F1) in ref. 14]. At higher temperatures (690–710, 710–730 and 730°C, respectively) the suitable kinetic models involve the reactions at phase interfaces [of circular or cylindrical symmetries; eqns (R2) and (R3), respectively, in ref. 14] as the limiting process. The process based on three-dimensional diffusion does not become operative until above 710°C, or 730°C for ZrO_2-7, the corresponding equation being that given by Zuravlev–Lesochin–Tempelman (ZLT[31]) or, at higher temperatures, that by Jander [eqn (D3) in ref. 14]. The respective temperatures for ZrO_2-S are 730 and 760°C and for CRO-1 760°C.

CONCLUSION

The reaction of formation of the blue zircon pigment represents a mildly exothermic process ($-\Delta H \sim 17$–$20\,\mathrm{kJ\,mol^{-1}}$). Several mechanisms operate in the pigment formation. With increasing calcination temperature, the governing process shifts from random nucleation to reactions at phase interfaces and finally (at the higher temperatures used in practice) to the processes based on three-dimensional diffusion. The component which predominantly diffuses is the silicate component, in two ways: up to 850–900°C in the form of alkali silicate (or vanadate–silicate) melt, and above this temperature in the form of silicon tetrahalide. Also mobile is the vanadate component, in the form of a melt of sodium vanadate bronzes (at lower temperatures) or in the form of gaseous oxide–halide. The zirconium(IV) component is also transported, but only to a very low extent (in this respect it is important that an intermediate of the type of zirconium(IV) divanadate is formed). The oxygen released from the chromophore has favourable mineralization effects which complement the function of the sodium halogenide mineralizers. The decisive part of the oxygen is released from the chromophore during the exothermic pigment formation proper.

Of the three zirconium(IV) oxides studied, the ZrO_2-7 sample, which is of mineral origin, was found to possess the highest reactivity, in contrast with the other two samples, which are synthetic. This is due to the structure of the mineral oxide, i.e. to the large number of defects (and vacancies) which enable an easier participation of this oxide in the synthesis reactions. Therefore, the pigment synthesis reactions from ZrO_2-7 start at a temperature 35–60°C lower than the other samples, and the individual changes of the governing mechanisms are also 30–50°C lower, whilst the exothermicity is somewhat higher (by 1·6 and 3·2 kJ mol^{-1}, respectively). The rate constant values of the individual kinetic equations are also highest with this oxide.

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