

Inhibition of the Anatase—Rutile Phase Transformation with Addition of K_2O , P_2O_5 , and Li_2O *

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Dedicated to the 80th birthday of Professor Elemír Kossaczký

During the sulfate process of TiO_2 pigment production, hydrated titanium dioxide is calcined. As a result of the polymorphous conversion, rutile is obtained. Roasting additives are introduced into the calciner, in order to achieve required process temperature, crystallite size of individual phases, optical properties, and the pigment photostability.

Calcination process was investigated on the laboratory scale with the use of hydrated titanium dioxide containing rutile nuclei from the industrial installation. The influence of both temperature and calcination time on the anatase—rutile transformation ratio and the crystallites growth was determined. The obtained dependences were described using exponential equations. The ratio of anatase—rutile transformation was higher at elevated temperatures. It was noticed that the process temperature affects the conversion ratio considerably more than the calcination time.

During the experiments alkaline metals (potassium, lithium) and phosphate were introduced into the calcination suspension. It was noted that the increase of phosphates content in the calcinated $TiO_2 \cdot nH_2O$ (0.1—0.5 mass % P_2O_5 in relation to TiO_2) caused the anatase—rutile transformation ratio to drop 2 to 10 times. Moreover, the phosphates presence restricted an unfavourable anatase and rutile crystallites growth. In fact, their crystallites size was 2—3 times lower, compared to the crystallites size measured when the phosphates were not added. If the potassium content in hydrated TiO_2 was increased (0.05—1.0 mass % K_2O in relation to TiO_2), during calcination the rutile formation passed through a maximum. Similar behaviour was observed when lithium (0.025—0.5 mass % in relation to TiO_2) was introduced instead of potassium. Neither anatase nor rutile average crystallites size was influenced by the potassium or lithium addition.

Owing to its properties titanium dioxide is employed on a wide scale in chemical industry as a pigment and catalyst [1—6]. It also finds application in the production of ceramics, in the process of solar exploitation and environment remediation. Titanium dioxide is chemically stable, nonvolatile, noncombustible, nontoxic compound characterized by a high refractive index. These qualities make TiO_2 widely applicable as a pigment for paint and varnish, plastics, paper, rubber, ceramics, pharmaceutical, food, and cosmetics industries. Moreover, TiO_2 has a high dielectric constant and is oxygen-susceptible. In 2003 global titanium dioxide production amounted to 4.8×10^6 t.

Titanium dioxide can be observed in three polymorphous modifications: anatase (tetragonal system),

brookite (orthorhombic system), and rutile (tetragonal system). Rutile boasts the highest thermodynamic stability. Anatase is produced *via* sulfate process and rutile by sulfate or chloride processes. Some titanium dioxide properties are heavily dependent on its crystallographic structure. Rutile is characterized by a higher density, atoms fraction in the structure, substantial hardness, and refractive index. Meanwhile, the pigment properties of rutile prevail over those of anatase, the latter modification is more suitable as a catalyst.

While heating TiO_2 to a temperature exceeding $400^\circ C$, an irreversible change, yellowing, takes place. This is due to the crystal lattice expansion, recrystallization accompanied by the formation of rutile nuclei and the crystallites growth. Along with the mentioned

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phenomena, a simultaneous decline of titanium dioxide specific surface can be observed. Specific surface area of titanium dioxide pigments, depending on their application, ranges from $0.5 \text{ m}^2 \text{ g}^{-1}$ to $300 \text{ m}^2 \text{ g}^{-1}$.

Chemical composition of TiO_2 pigments depends on the production method, the raw material used, and on the purpose for which the pigment was manufactured. Hydrolysis of titanium(IV) sulfate, purification of hydrated titanium dioxide, its calcinations and surface treatment are the most important factors influencing the quality of TiO_2 generated by the sulfate process. Even after its purification, the hydrated TiO_2 used for calcination still contains sulfuric acid, sulfates and other impurities coming from the raw material and particular stages of its processing. During titanium dioxide calcination several physical and chemical processes take place. Hydrated TiO_2 is dried, dehydrated, and submitted to dehydroxylation and desulfurization. Simultaneously, crystallization, anatase crystals growth, as well as the anatase—rutile transformation occurs. The polymorphous transformation may be conducted at a wide range of temperatures $400\text{--}1100^\circ\text{C}$, though normally it takes place at about $800\text{--}850^\circ\text{C}$.

Also anatase—rutile transformation is influenced by the anatase preparation procedure, its particle size, by the calcination temperature and time, addition of the conversion promoters or inhibitors, and also by the presence of rutile nuclei [1—6]. These factors are used to control the transformation and to design the product's specific phase composition and its optical characteristics [1—10]. By introducing aluminium, potassium, phosphorus, sulfur, silicon, lanthanum, cesium, and zirconium compounds the transformation temperature could be changed [1—10]. Phosphates limit considerably the growth of both TiO_2 phases' crystallites [2, 9]. Li_2O , ZnO , MgO , Sb_2O_3 , and rutile nuclei accelerate the anatase—rutile transformation [1, 2, 5—10]. However, it is worth mentioning that the conclusions regarding the activity of particular additives acting as promoters or inhibitors of "rutilization" are sometimes contradictory. The influence the additives exert depends on their nature, stability, distribution, and the amount used during the TiO_2 transformation. Particles of additives present on the titanium dioxide surface limit the growth of crystallites during the calcinations process and increase the temperature of the anatase—rutile transformation, whereas the ones dissolved in the TiO_2 bulk accelerate it [2, 9]. In the anatase—rutile phase transformation, rutile nucleates at the interface, on the surface and in the bulk [7]. The predominant nucleation mode may change from interface nucleation at low temperature to surface nucleation at intermediate temperatures and to bulk nucleation at very high temperatures. The particular mode fraction depends on the particle packing and the calcination time. It has been found [9] that additives causing vacancy in the titanium dioxide anion sub-

lattice (Li^+ , K^+ , Cu^{2+} , Al^{3+}) act as promoters of the anatase—rutile transformation, whereas additives reducing the number of vacancies (S^{5+} , P^{5+} , Nb^{5+}) are responsible for the transformation inhibition.

Additives can improve the pigment optical characteristics considerably, as this parameter is strongly influenced by the TiO_2 crystallites size [2, 11]. On the other hand, additives presence may influence negatively the product photostability [2, 11]. At given temperature, promoter increases the anatase—rutile conversion only up to a certain promoter content. If the additive content in the calcined TiO_2 is further increased, the transformation rate is either not affected by this parameter, or decreases.

The aim of the present research was to determine the influence of the calcination temperature and time, as well as the modifying agents (*e.g.* potassium, phosphorus, and lithium compounds) content on the degree of the polymorphous anatase—rutile transformation and the average crystallite size of generated phases.

EXPERIMENTAL

During experiments hydrated titanium dioxide containing 3—3.5 mass % of rutile nuclei in relation to TiO_2 was used. This suspension was obtained by bleaching the raw TiO_2 in an industrial installation. Table 1 presents the content of some impurities in the three calcined samples of hydrated titanium dioxide. Prior to calcination, the suspension was doped with solution containing chosen amount of an appropriate modifier. Phosphates were introduced as $\text{NH}_4\text{H}_2\text{PO}_4$, potassium as K_2SO_4 , and lithium in the form of Li_2SO_4 . Prepared samples were calcined in the laboratory muffle furnace at a preset temperature ranging from 650 to 900°C . The calcination time was varied from 1 to 5 h.

The X-ray diffraction analysis was used to determine the anatase and rutile content and the crystallites size in the calcined titanium dioxide samples (X'Pert PRO Philips). The average size of crystallites was determined on the basis of Scherrer's equation [12]. The crystallites average size variation and the relative abundance of anatase and rutile phases were calculated from the (101) reflection of anatase and the (110) reflection of rutile. The width of the peak at half maximum was calculated taking into account the

Table 1. Impurities Content in Hydrated Titanium Dioxides

	<i>w/mass %</i>				
	Fe	Mg	Si	Na	K
HTD1	0.288	0.025	0.195	0.142	0.153
HTD2	0.326	0.035	0.245	0.126	0.076
HTD3	0.057	0.040	—	0.018	—

so-called apparatus broadening. This parameter was determined on the basis of the sample of coarse crystalline silicon.

RESULTS AND DISCUSSION

In the first series of experiments, the influence of the calcination time and temperature on the anatase—rutile transformation ratio and the average size of the generated crystallites was determined. Two samples of hydrated titanium dioxide (HTD1 and HTD2, Table 1) were calcinated. It was found that depending on the physicochemical properties of the hydrated titanium dioxide suspension (the impurities content depends on the brand of raw material used), the measured transformation ratio at 700 °C, 750 °C, and 800 °C (calcination time 1 h) was 0–5 %, 8–50 %, and 70–97 %, respectively. By increasing the calcination time to 5 h, the transformation ratio reached 76–81 % at 750 °C. However, when the calcination temperature was 650 °C, the conversion increase was less important, only about 13 %.

It was noted that the conversion is more affected by the temperature than the time of calcination. The variation of the transformation ratio of anatase to rutile with the calcination time at 750 °C for HTD1 and HTD2 was described by the Avrami equation

$$\alpha = 1 - \exp(-kt^n) \quad (1)$$

α being the anatase conversion to rutile, k rate constant of transition, n parameter specific to the reaction investigated, and t the calcination time. In Table 2 the calculated k and n constants are shown. The values of these coefficients depend on the kind of calcined material. The rate constant of the anatase—rutile transformation proved to be lower when hydrated titanium dioxide containing higher amount of potassium (0.153 mass %) was calcined. The above relationship is shown in Fig. 1.

Simultaneously, a change of the average crystallites size, both of anatase and rutile phases, was observed. It was found that the change of this parameter varied with the calcination temperature and time. At 650 °C the crystallite size growth was insignificant, moreover, the anatase—rutile transformation ratio was negligible and the only crystalline phase observed was anatase. After 5 h of calcination at the temperature of 650 °C, the anatase crystallite size changed from 20 nm to about 74 nm. When this experiment was conducted at 750 °C, about 2 times bigger anatase crystallites were observed compared to those found at 650 °C. Moreover, the rutile phase crystallites formed by the polymorphous transformation were 2–4 times bigger compared to anatase crystallites.

Based on these results, variation of the average crystallite size (D) of both, anatase and rutile, with time was modelled. For this purpose, the equation pro-

Table 2. Parameters of the Avrami Equation and the Crystallites Growth Model for Selected Experiments of the Anatase—Rutile Transformation

	$T/^\circ\text{C}$	k	n	a	b
HTD1	750	0.4106	0.8696	309.6776	0.3536
HTD2	750	0.5826	0.6725	250.6908	0.2813
HTD1	650	–	–	53.5575	0.2361
HTD2	650	–	–	49.1283	0.2229

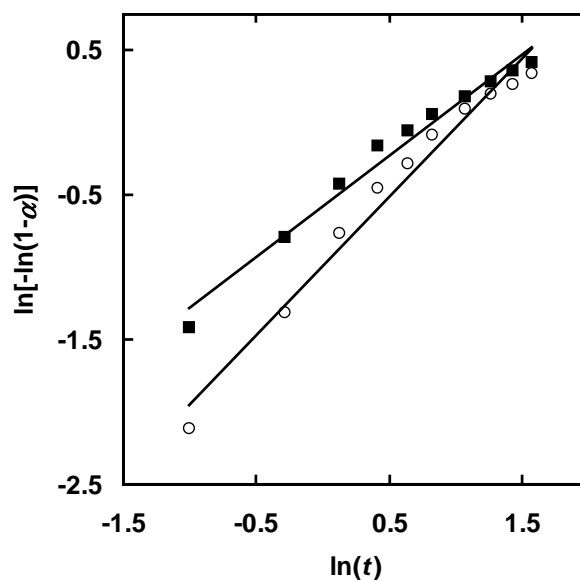


Fig. 1. Variation of anatase to rutile conversion with time of the isothermal calcination at 750 °C. HTD1 – 0.153 mass % (○) and HTD2 – 0.076 mass % (■) of potassium in hydrated titanium dioxide.

posed in earlier studies was used [1, 2]

$$D = at^b \quad (2)$$

where a and b are the model parameters.

Table 2 shows the calculated values of parameters a and b . These values were mostly influenced by the calcined material composition. The values of parameter b are shown to be directly proportional to the potassium content as well as the process temperature.

Fig. 2 summarizes the experimental and fitted crystallite growth of anatase at 650 °C and of rutile at 750 °C with the calcination time.

During the next experiments, samples of hydrated titanium dioxide (HTD3, Table 1) doped with phosphates were prepared. The amount of P_2O_5 in the sample varied from 0.1 to 0.5 mass % in relation to TiO_2 . By increasing the phosphates content in the $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ samples, the anatase—rutile transformation ratio declined 2–10 times. That influence was more or less clearly depending on the temperature

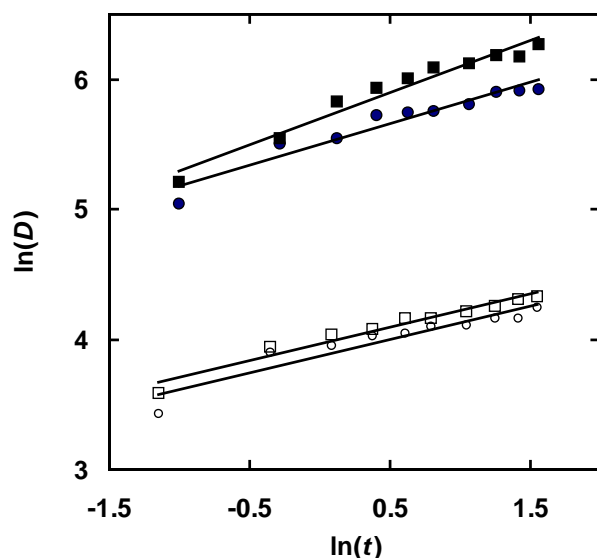


Fig. 2. Influence of the isothermal calcination time on the crystallites average size of anatase (opened symbols) and rutile (full symbols) at 650 °C (○, □) and 750 °C (●, ■). HTD1 (□, ■); HTD2 (○, ●).

Table 3. Influence of Phosphates Content on the Anatase—Rutile Transformation and the Average Size of Anatase Crystallites

$w_{\text{P}_2\text{O}_5}/\text{mass \%}$	$w_{\text{anatase}}/\text{mass \%}$	$D_{\text{anatase}}/\text{nm}$
0	30	>1000
0.1	52	480
0.25	88	380
0.5	94.9	290

and time of the calcination process. The inhibition of anatase—rutile transformation ratio was less noticeable when the temperature and the calcination time were higher. Table 3 presents the anatase content and the crystallite size variation with the initial phosphate content after the sample calcination at 750 °C for 2 h.

It can be concluded that the addition of phosphates inhibits the unwanted growth of anatase and rutile crystallites during the sample calcination (Table 3). Crystallites size of samples calcined in the presence of phosphates was 2—3 times lower than the size of those generated by calcining the original $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ suspension.

During the next series of experiments, samples containing 0.05—1.0 mass % of K_2O (in relation to TiO_2) in the suspension of hydrated TiO_2 (HTD3, Table 1) were prepared. By increasing the amount of potassium the rutile content in calcined sample passed through a maximum. The increase of the transformation ratio rate was observed for the K_2O content in hydrated TiO_2 lower than 0.2 mass %. Variation of the anatase conversion with the added potassium amount was in-

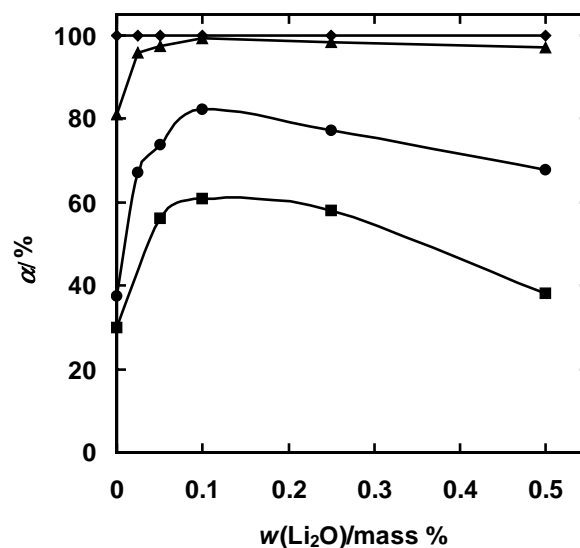


Fig. 3. Influence of the lithium content on the anatase—rutile transformation measured at different experimental conditions: 700 °C, 4 h (■); 750 °C, 2 h (●); 800 °C, 1 h (▲); 900 °C, 1 h (◆).

fluenced also by the calcination temperature and time. The influence of potassium addition on the anatase—rutile transformation turned out to be more noticeable at lower process temperatures. No effect of the roasting additive on the average size of crystallites of the reaction product phases was observed.

Addition of lithium exerted similar influence on the anatase—rutile transformation as that of potassium. The amount of lithium introduced into the suspension of hydrated titanium dioxide (HTD3, Table 1) corresponded to 0.025—0.5 mass % of Li_2O (in relation to TiO_2). Again, the increase of lithium amount in the sample caused the anatase conversion to pass through a maximum at about 0.1 mass % of Li_2O in the dry sample. The results of experiments carried out at the different calcination temperatures and Li_2O contents are shown in Fig. 3. An important increase of anatase conversion to rutile provoked by the lithium addition was observed at lower calcination temperature.

Finally, a preliminary study dealing with the synergic effect of phosphates and potassium or phosphate and lithium additives on the polymorphous anatase conversion and the crystallites growth during TiO_2 calcination was carried out. Table 4 presents the results of hydrated titanium dioxide (HTD3, Table 1) calcination at 750 °C for 2 h. It was established that the influence, which lithium exerts over TiO_2 in the presence of phosphates is stronger than that of potassium, causing faster anatase to rutile transformation as well as the TiO_2 crystallites growth.

The inhibiting influence of phosphates on the anatase—rutile transformation results from the anion chemisorption model on the surface of the hydrated titanium dioxide [2, 7, 9]. Interface and surface rutile

Table 4. Influence of Potassium, Lithium, and Phosphates Content on the Anatase—Rutile Transformation and the Average Crystallite Size of Both Phases

$w/\text{mass } \%$	$\alpha/\%$	D/nm	
		Anatase	Rutile
None	38	220	390
0.15 P ₂ O ₅	19	170	300
0.1 K ₂ O	50	290	490
0.15 P ₂ O ₅ , 0.1 K ₂ O	15	200	230
0.1 Li ₂ O	82	360	610
0.15 P ₂ O ₅ , 0.1 Li ₂ O	31	230	360
0.22 P ₂ O ₅	9	150	180
0.2 K ₂ O	32	280	370
0.22 P ₂ O ₅ , 0.2 K ₂ O	10	190	160
0.2 Li ₂ O	77	460	650
0.22 P ₂ O ₅ , 0.2 Li ₂ O	15	250	250
0.5 P ₂ O ₅	5	120	120
0.5 P ₂ O ₅ , 0.2 K ₂ O	6	150	130
0.5 P ₂ O ₅ , 0.2 Li ₂ O	8	180	180

nucleation is limited. This influence is lower at the higher temperatures of the transformation where bulk nucleation prevails over the interface and the surface ones [7].

The influence of potassium and lithium on the anatase—rutile transformation results from their chemisorption on the surface of the hydrated titanium dioxide as well as from generating vacancy in the TiO₂ crystal lattice (Ti⁴⁺ substitution) [7, 9, 10]. However, potassium turns out to be adsorbed stronger than lithium. Lithium demonstrates a stronger than potassium tendency to increase the anatase—rutile transformation ratio. Compared with phosphates these metals have a much lower ability to be absorbed on the surface of the hydrated titanium dioxide [2].

The synergic influence on the anatase—rutile transformation of phosphates and potassium results from the precipitation of appropriate phosphates on the surface of the hydrated titanium dioxide [2, 9, 10]. Lithium, however, reduces their activity. It seems likely that the process of lithium phosphates precipitation is accompanied by the generation of vacancies as a result of titanium ions being substituted with the lithium ones.

The observed impact of particular additives on the anatase—rutile transformation might be certainly influenced by the initial content of these and other components/impurities (Fe, Mg) in the calcined material. Still, the results presented in this study show a clear variation of the phase transformation rate with the content of potassium, lithium, and phosphorus in hydrated titanium dioxide.

SYMBOLS

a, b	parameters of eqn (2)	
D	average size of crystallites	nm
HTD	hydrated titanium dioxide	
k, n	parameters of eqn (1)	
T	Temperature	°C
t	time	h
w	component content referred to a dry sample	mass %
α	anatase conversion to rutile	

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