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ISOTHERMAL DESORPTION OF WATER FROM ANATASE

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The variation in the water content of anatase was studied as a function of the equilibrium water vapour pressure in the range from 2660 Pa to 0.0013 Pa at 295 K. It was found that anatase contains at most 2.68 mole of physically adsorbed H_2O per mole of TiO_2, with an additional 0.34 mole of H_2O per mole of TiO_2 which does not desorb even at 0.0013 Pa.

Hydrated titanium dioxide (HTD),, also called metatitanic acid, is an intermediate in the sulphuric method of obtaining titanium white. The aim of this paper was to establish the modes of water combination in HTD. The material studied was HTD manufactured in the chemical plant "Police". From this product, two samples were dried in air in ambient temperature (about 22°) and at 105°. Radiographs of the studied oxides were registered with an HZG-4c diffractometer, using $Cu_{K\alpha}$ radiation. The material of both samples was identified as anatase (Fig. 1).

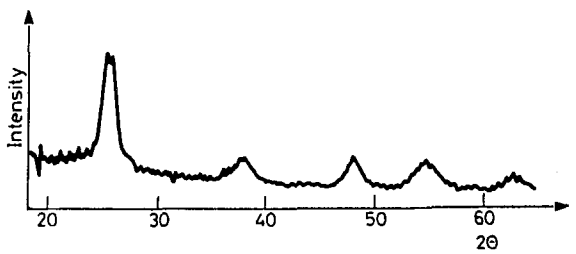

Fig. 1 Model radiogram of hydrated titanium dioxide (anatase [1])

An attempt was made to establish the compositions of these samples via thermal analyses and chemical determination of sulphur. Results are given

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in Table 1. Multiple analyses of composition showed that the conditions of drying the samples, the time passing after drying, but also the temperature and environmental humidity, all significantly influence the water content of anatase.

Table 1 Composition of HTD dried under various conditions

Drying temp., °C	Weight, %			Molar composition		
	TiO_2	H_2O	SO_3	TiO_2	H_2O	SO_3
22	81	13.33	5.67	1	0.73	0.07
105	86.02	7.95	6.03	1	0.41	0.07

Experimental

Studies of water desorption from HTD were conducted at 295 K in a vacuum apparatus equipped with quartz scales with a weighing sensitivity of 200 mm/g. The positions of indicating points on the two parallel scales were read off by means of a cathetometer accurate to 0.01 mm. After the HTD was placed in the apparatus in the presence of water, the air was evacuated to the pressure of saturated water vapour (p_o) and measurements were make. Desorption of water was studied within the range from 2660 Pa (p_o) to 0.0013 Pa. The stable, unchanging mass of HTD at 0.0013 Pa was accepted as the mass of the adsorption agent and was called the vacuum-dry mass. Next, water vapour was introduced and the increase in the sample mass was observed; the mass achieved the initial value at p_o. The next decrease to 0.0013 Pa caused a decrease in the sample mass to the vacuum-dry mass. In the further experiments, the apparatus was aired and the sample mass was observed for a few days. It was observed that the sample mass varied with the air temperature and humidity. This "air-dry sample" was analysed by thermal and chemical analysis in order to establish its composition.

Discussion

Problems of H_2O - TiO_2 interactions have been discussed in many experimental studies and reviews [2]. Primarily of importance are the studies of the correlation between the HTD composition and the pressure of water vapour under isothermal conditions [3-7]. These studies and also reports on

the applications of thermal analysis and temperature-programmed desorption (TPD) [8] prove that the water in HTD may be bound weakly and strongly. At present, therefore, it seems that the idea about the hydration of TiO_2 cannot be regarded as true; further the hypothesis that water occupies the free octahedral space of the anatase lattice [2] would require experimental confirmation of the sudden change of the character of the interactions at a TiO_2:H_2O mole ratio of 1:1. The present work revealed the monotonicity of the changes in HTD mass as far as the water vapour pressure is concerned (Fig. 2) and the course of the water desorption isotherm (Fig. 3) is typical of polymolecular physical adsorption.

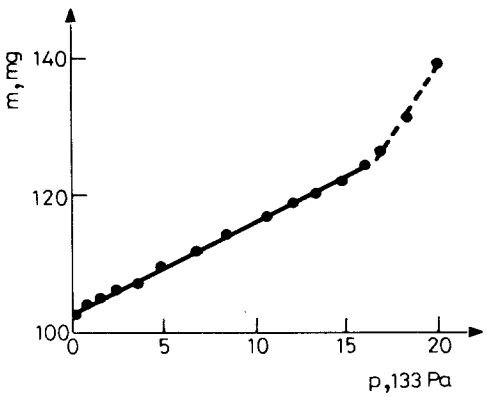

Fig. 2 Relationship between change in mass of anatase and pressure of water vapour

Table 2 Compositions of samples subjected to desorption-adsorption

Sample	Mole composition
vacuum-dry	$TiO_2 \cdot 0.34H_2O \cdot 0.07SO_3$
air-dry	$TiO_2 \cdot 0.73H_2O \cdot 0.07SO_3$
in equilibrium with saturated water vapour	$TiO_2 \cdot 3.02H_2O \cdot 0.07SO_3$

On the basis of the composition of the air-dry sample, the molecular compositions of HTD at the isotherm extrema were calculated. The data in Table 2 demonstrate that 1 mole of TiO_2 can combine with (3.02–0.34 =) 2.68 mole of physically adsorbed H_2O. Under conditions of incomplete saturation with water vapour, HTD can both absorb and lose water, the composition therefore displaying great instability. Theoretical studies [9] indicate that the number of sites able to chemisorb water

depends on the size of the anatase grain and on the proportions of the most readily formed planes. For grains with a diameter of 10 nm, there can be $0.34\text{-}6.023 \cdot 10^{23}$ water - binding sites per mole of TiO_2.

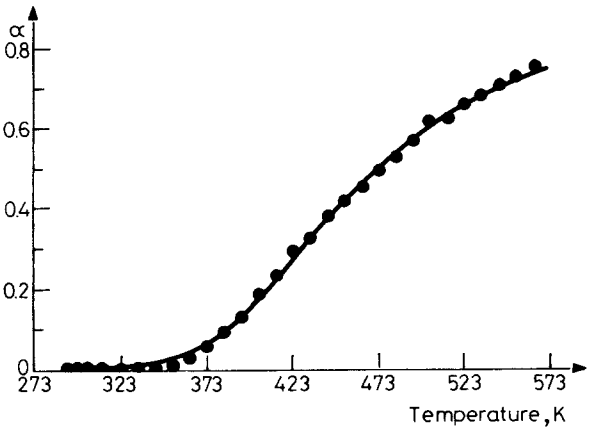

Fig. 3 Isotherm of water vapour desorbed from anatase. *a* - adsorption expressed in grams of water per gram of adsorbed agent, p/p_o - relative pressure

Conclusions

1. Hydrated titanium dioxide (HTD) produced in Poland contains up to 2.68 mole of physically adsorbed H_2O per mole of TiO_2 at 295 K.
2. The ready adsorption-desorption of water within this range (up to 2.68 mole of H_2O) is the reason for the unstable composition of HTD under ambient conditions.
3. HTD produced in Poland contains 0.34 mole of more strongly combined H_2O per mole of TiO_2 at 295 K.
4. Theoretical studies demonstrate that, for "pigment"-sized grains, the number of active sites on the anatase surface is enough for the whole water content to be strongly chemisorbed.

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Zusammenfassung – Bei einer Temperatur von 295 K wurde die Veränderlichkeit des Wassergehaltes von Anatas mit einem Ausgleichsdruck zwischen 2660 Pa und 0.0013 Pa untersucht. Es wurde festgestellt, daß Wasser in Anatas teilweise durch unterschiedlich starke physikalisch Adsorption gebunden ist.