BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 243—244 (1969)

Contact Potential in Vacuum for Titanium Dioxide Powder

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(Received March 15, 1968)

Titanium dioxide is well-known as a pigment. It is considered that the chalking phenomena of titanium dioxide paint have something to do with the behavior of adsorbates on the pigment surface. In the case of zinc oxide, both the photoelectric and the thermoelectric work function have already been determined by measurements of the external photoelectric effect[1)] and contact potential[2)] respectively, while the behavior of adsorbates has been considerably clarified by many experimental results.[3)] However, in the case of titanium dioxide, the surface potential and the surface photovoltage have not been studied, and the behavior of adsorbates has not been clarified as yet. Hence we measured changes in the contact potential and the surface photovoltage of titanium dioxide powder by changing the atmosphere around the layer. These phenomena have significance especially in discussing the surface behavior of titanium dioxide powder.

Experimental

Titanium dioxide powder, which is of a special grade (the impurities are given as follows: Fe$<$0.001%, Pb$<$0.002%, As$<$0.0005%) and the crystal size of which is about 0.1—0.5μ, was dispersed in alcohol and spread uniformly on a 7×7 cm^2 aluminum plate. These specimens were dried at 100°C for 2 hr, and then left in a dark chamber for 48 hr or more. These layers were between 15 and 25 μ thick. The contact potential was measured by the Kelvin method using a nesa glass electrode. The sample was placed in a vacuum vessel, in which there was silicone grease and where a diffusion pump was used. The nesa glass electrode was vibrated by an oscillator at 1 kc/sec. The specimen was exposed to a tungsten lamp without any filters. All the measurements were made at room temperature by the following procedures. After the air in the vessel had been slightly evacuated, the pressure was kept at a given pressure for 2 hr. When the surface potential reached a stable value, we measured the surface potential. The pressure range studied was from normal air pressure to 10^{-5} mmHg. After evacuation to 10^{-5} mmHg, foreign gas was introduced into the system, and the photovoltage of the layer was measured by illuminating the sample surface with a white light of 480 lux.

Results

Figure 1 shows the curves of the surface potentials of rutile and anatase in the dark against the air pressure. The dotted line represents the potential of gold, which corresponds to the work function of 4.8 eV. It may be seen that the surface potential of rutile has a minimum at a pressure around 40 mmHg, and that the surface potential increases with the decrease in air pressure between 10 and

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10^{-4} mmHg, gradually reaching 50—100 mV above the Au-potential at a pressure of 10^{-5} mmHg. The surface potential of anatase was about 400 mV higher than that of the rutile layer in atmospheric air, and monotonously increased with the decrease in air pressure.

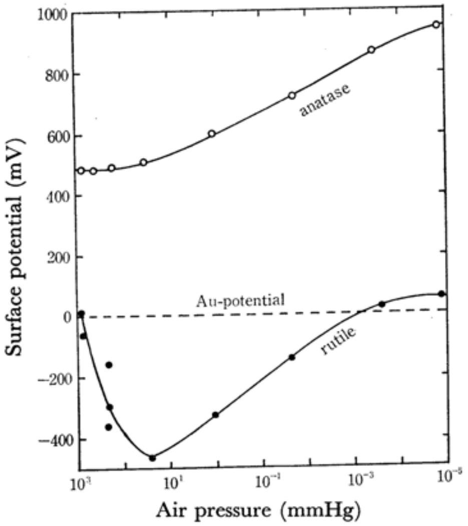

Fig. 1. Surface potential of the rutile and anatase layers in the dark against the air pressure.

In Fig. 2, the surface photovoltages of the rutile layer in various ambients are shown. On irradiation, a large photovoltage, 500 mV, was observed with a quick response in the vacuum of 3×10^{-4} mmHg. However, in dry air at normal pressure, the photovoltage amounted to 240 mV. Moreover, in wet air (relative humidity of 75%), the photovoltage has a very small value, 30 mV.

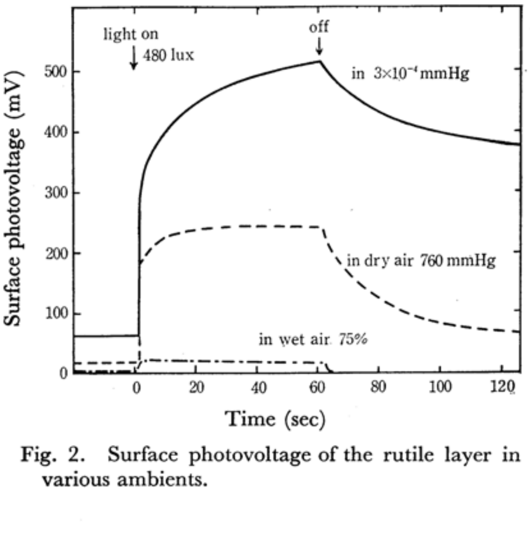

Fig. 2. Surface photovoltage of the rutile layer in various ambients.

Discussion

The adsorbates on the titanium dioxide surface at normal air pressure are considered to be oxygen and water. It has been recognized by ESR that oxygen chemisorbs on the titanium dioxide surface as a negative ion, O_2^-.[4] Therefore, if the air pressure around the layer is decreased, the adsorption equilibrium of oxygen slightly deviates from that at the normal air pressure. Then the surface potential increases with a decrease in air pressure. On the other hand, the behavior of water on the titanium dioxide surface has not yet been clarified. However, in the case of zinc oxide, the behavior of water on the surface has been studied to some extent, and it has been recognized that water chemisorbs on the zinc oxide surface donatively.[5] We assume that the same is the case with titanium dioxide. Therefore, the surface potential decreases if water desorbs from the surface. Figure 1 shows that the change in the surface potential of rutile resembles that of zinc oxide.[6] Therefore, the change in the surface potential of rutile in Fig. 1 means that the water on the surface desorbs first; after that, a part of the oxygen gradually desorbs from the surface. On the basis of these results only, we can not determine the absolute work function of titanium dioxide, because some other adsorbates remain on the suface even at the pressure of 10^{-5} mmHg. In the case of anatase, the minimum peak is not observed. This fact can not be explained easily on the basis of these results only.

The photovoltages observed under the illumination of a white light may be attributed to the desorption of oxygen. Therefore, these phenomena greatly depend on the ambient atmosphere around the layer. In the case of a vacuum of 3×10^{-4} mmHg, the photovoltage reaches a value as high as 500 mV. In wet air, however, the photovoltage greatly decreases. These phenomena indicate that the surface of titanium dioxide is greatly affected by the adsorption of water. Moreover, the rate of the dark decay of the surface photovoltage is slow in a vacuum, but quick, at normal air pressure. It may be said that the rate of the readsorption of oxygen, which is desorbed by light, is low in a vacuum and high at normal air pressure.

The authors wish to thank Mr. Isao Tashiro of the Rikoh Co., Ltd., for giving many useful suggestions about the measurement of the contact potential.

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