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Optical properties and radiation stability of TiO_2 powders modified by Al_2O_3, ZrO_2, SiO_2, TiO_2, ZnO, and MgO nanoparticles[☆]

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ABSTRACT

The high-temperature modification of micron-sized grains of titanium dioxide with nanoparticles of Al_2O_3, ZrO_2, SiO_2, TiO_2, ZnO, and MgO was performed. The influence of these types of nanoparticles on the diffuse reflectance spectra of modified pigments in the range of 350–2000 nm and their changes after irradiation by 30 keV electrons were investigated. It was determined that the modification does not lead to significant changes in the diffuse reflection spectra of the TiO_2 pigments. The type of oxide nanoparticles, the size of the ionic radii and the valence of the cations do not noticeably influence the radiation stability of the modified pigment, as determined by the intensity of the absorption bands in the visible and near infrared regions of the spectrum. The determining factor in the increase of the radiation stability of the modified pigments is the specific surface area of the nanopowders.

1. Introduction

Titanium dioxide powders are widely used in various fields of science, technology and industry as photocatalysts [1–4], thermal control coating pigments and anti-reflection coatings of spacecraft [5,6], photovoltaic solar cells [7–10], and pigments for household paints. Increasing their light stability and radiation stability is an important task. One of the methods used for this purpose is to create layers of nanoparticles on the surface of the grains and granules of the pigments. The nanoparticles in this case act as centers for relaxation of the initial defects created by the irradiation. Furthermore, they absorb part of the incident radiation. When their stability to radiation is higher than that of the pigment particles, they reduce the degradation of the properties.

Nanoparticles can enhance and influence the original optical properties of the pigments. The main characteristic of white pigments and paints is a diffuse reflectance spectrum (ρ_λ) in the solar range. The reflectance spectra are determined by photon scattering and absorption. Because the sizes of nanoparticles are similar to the range of ultraviolet wavelengths of the solar spectrum, the modification can influence the scattering of photons in this spectral region.

The absorption of photons is determined not only by the presence of impurities (purity) and the stoichiometry of the nanopowders (anionic and cationic vacancies and interstitial atoms and ions) but also by their size (r) and specific surface area (S_{sp}) [11,12]. These dimensional characteristics determine the sorption processes, and the concentration of gas molecules chemisorbed on the surface of pigments depends on their values. Molecules and atoms of oxygen, molecules of CO, CO_2, H_2O and OH^- groups absorb light in the near-IR and UV regions [13–16]. Hence, the spectra ρ_λ and their change after irradiation ($\Delta\rho_\lambda$) will depend not only on the type of nanoparticles but also on their size and specific surface area.

Because the grain sizes of the pigments are in the range of hundreds of nanometers to several micrometers, they are comparable with the depth of penetration by photons in the solar spectrum and in the main part of the spectra of charged particles in space. Therefore, any dose of these types of radiation will affect the absorption spectra of the pigments; however, the effect will appear more intensely at the beginning of the irradiation, when the color centers (CC) are formed on the preradiation defects. Such preradiation defects are: 1) intrinsic defects of stoichiometry, 2)

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impurity defects, and 3) molecules and radicals adsorbed on the surface.

The aim of this work is to study the influence of the type of metal oxide nanoparticles, as well as the size of the grains and the specific surface area, on the diffuse reflectance spectra and changes in the spectra after irradiation with accelerated electrons for modified titanium dioxide pigments.

2. Experimental

In these studies, TiO_2 powder (Kronos 2059, rutile) for industrial production was used. The average particle size was 240 nm, and the specific surface area was 7.5 m^2/g. The nanopowders were obtained via the plasma-chemical method [16]. The types of oxide nanopowders were selected such that the relationships among them were (Table 1):

- with pronounced dielectric (Al_2O_3, ZrO_2, SiO_2, MgO) and semiconductor (ZnO, TiO_2) properties;
- cations of these compounds should have a different charge: 4 – Zr^{4+}, Si^{4+}, and Ti^{4+}, 3-Al^{3+}, 2 – Mg^{2+} and Zn^{2+};
- the ionic radii of the cations must be greater than (0.74 Å – Zn^{2+}, 0.72 Å – Mg^{2+}, 0.84 Å – Zr^{4+}) and less than (0.54 Å – Al^{3+}, 0.4 Å – Si^{4+}) and the ion radius of Ti^{4+} must be equal to 0.68 Å [17];
- in addition to the five nanopowders with cations doped by diffusion into the TiO_2, the effect of modifying nanoparticles with their own cations Ti^{4+} was investigated.

The average grain sizes of the nanoparticles (in nm) were: Al_2O_3 – 30, ZrO_2 – 30, ZnO – 50, MgO – 60, SiO_2 – 55, and TiO_2 – 60. The specific surface areas of the powders (in m^2/g) were: Al_2O_3 – 49, ZrO_2 – 25, ZnO – 20, MgO – 26, SiO_2 – 60, and TiO_2-26. All the nanopowders have a crystalline structure. An exception was the SiO_2 powder, which was amorphous, leading to a high porosity and a large surface area. Photographs and XRD patterns of the nanopowders are shown in Figs. 1 and 2.

Rutile (TiO_2 powder) with an average grain size of 240 nm and a specific surface area of 7.5 m^2/g was used as the starting material for the modification procedure. The TiO_2 powder (2 g) was mixed with the various metal oxide nanoparticles in a ratio of 100:7 wt.%. Distilled water (50 mL) was added to assist the mixing using a magnetic mixer. The water was then evaporated by heating at 150 °C for 6 h. The mixture was heated in a muffle furnace for 2 h at 800 °C. The mixture was then ground in an agate mortar and pressed into the metal substrate with a diameter 24 mm and a height of 2 mm. The modifying modes are selected based on the results of previous studies on the effects of the concentration of SiO_2 nanoparticles and modifying temperature on the optical properties and radiation stability of TiO_2 powders [18,19]. The prepared samples were mounted in the installation "Spectrum" [20] for measuring the diffuse reflectance spectra and for irradiation with accelerated electrons ($E = 30$ keV, $F = 2 \cdot 10^{16}$ cm^{-2}). The measurements were carried out in vacuum (*in situ*).

Table 1
Characteristics of the various oxide nanopowders.

Type of powder	$mTiO_2$	Nanopowders					
		ZnO	MgO	TiO_2	Al_2O_3	ZrO_2	SiO_2
Cation radius, Å	0.68	0.74	0.72	0.68	0.54	0.84	0.4
Cation charge	4+	2+	2+	4+	3+	4+	4+
Particle size, nm	240	50	60	60	30	30	55
Sp. surf. area, m^2/g	7.5	20	26	26	49	25	60

The value of the integral absorption coefficient of solar radiation a_s is calculated in accordance with ASTM standards (E490-00a and E903-96) by the formula:

$$a_S = 1 - \rho_S = 1 - \frac{\int_{\lambda_1}^{\lambda_2} \rho_\lambda I_\lambda d\lambda}{\int_{\lambda_1}^{\lambda_2} I_\lambda d\lambda} \qquad (1)$$

where

ρ_s is the integral reflectance of solar radiation;
$\rho_{\lambda-}$ is the spectral reflectance of the material;
I_λ is the spectrum of solar radiation;
$\lambda_1 - \lambda_2$ is the wavelength range of the solar radiation spectrum.

3. Results and discussion

3.1. The diffuse reflectance spectra of modified pigments

The modification of the pigments has a notable effect on their spectra ρ_λ in different wavelength regions (Fig. 3). An analysis of the changes in the reflectance characteristics was performed using the reflectance maxima appearing in the spectrum absorption bands at 440 and 580 nm in the visible region and at 850, 1200 and 1800 nm in the near infrared region (Fig. 4). In the range near 440 nm, the reflectance of heated and modified powders is increased by 2–3% (Table 2). An exception is the powder modified by nZnO, for which the value of ρ_λ is reduced by 2.4%. Near 580 nm, the reflectivity increases only in powders modified by nMgO and $nTiO_2$. For other modified powders, the reflectivity does not appreciably change; for the powder modified by ZnO nanoparticles, the reflectivity is also reduced.

In the near infrared region at 850 nm, the value of ρ increases significantly for powders modified by nMgO, $nTiO_2$ and $nSiO_2$. For other modified and warmed powders, ρ does not differ significantly. At 1200 nm, an increase of ρ is manifest in the spectra of powders modified by nMgO, $nZrO_2$, nZnO and $nSiO_2$. The greatest increase is 4%. Near 1800 nm, an increase of ρ both during heating and during every modification of the nanopowders is observed. The highest value of 4.7% was recorded for the powder modified by nZnO.

Thus, the heating of the TiO_2 powder to 800 °C does not result in significant changes in the reflectance across the spectrum from 350 to 1200 nm. In the region from 1200 nm to 2000 nm, the reflectance is increased by 4% or more. Modification by nanoparticles leads to an increase in the TiO_2 powder reflectance across the spectrum from 350 to 2000 nm. The increase reaches 2–3% in the visible region, and in the near-IR region, it is as much as 4.7%. For the variety of nanopowders, the magnitude of the increase differs. Compared with heating to 800 °C, the increase in the reflection coefficient of each of the modified powders is not more than 2–3%.

Changes in the spectra of the diffuse reflectance of the powders after modification can occur because the reflection coefficient of the nanoparticles differs from the reflectance coefficient of the micropowder. This difference is determined by the larger value of the scattering coefficient of the nanoparticles compared to that of grains of micron size and appears mainly in the visible region of the spectrum.

As was shown by experimental studies [18,21], the other reason for the difference of the reflection coefficient is the desorption of gas molecules from the surface during heating, the main components of which are OH-groups and water molecules. Such