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Photostability of Reflecting Coatings Based on the ZrO_2 Powders Doped with $SrSiO_3$

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The effect of doping with $SrSiO_3$ in the range of 1 to 17.5 mass % on the reflectance spectra and integral solar absorptance factor of ZrO_2 powders and their stability at ultraviolet irradiation were investigated. It was founded that the powders doped with 1 mass % of $SrSiO_3$ possess the greater photostability. Two types of thermal control coatings were fabricated. The first one was based on the undoped ZrO_2 pigment and the second one was based on the ZrO_2 pigment doped by 1 mass % of $SrSiO_3$. The comparative investigations of their optical properties and photostability show that the coating based on doped pigment is more effective than the coating with undoped pigment. The prediction of optical properties degradation for these coatings was made for a lifetime of 10 years according to obtained data. This prediction may be used for altitudes of 600–800 km, for which the main damaging factor is ultraviolet radiation of the sun.

Nomenclature

a_s = integral solar absorptance factor
E_{abs} = absorption energy
E_g = material bandgap
E_s' = radiation intensity
t = period of orbital flight, h
Δa_s = change in integral solar absorptance
$\Delta\rho$ = change in diffuse reflectance
$\Delta\rho(\lambda)$ = change in diffuse spectral reflectance ($\Delta\rho$ spectrum)
ε = thermal emittance
λ = wavelength
ρ = diffuse reflectance
$\rho(\lambda)$ = diffuse reflectance spectrum

Introduction

IT is known that zirconium dioxide powders have a wide bandgap ($E_g = 5.4$ eV at 300 K; Ref. 1) and that is why they are prospective pigments for reflective coatings in the range of the solar spectrum. In this regard, we may say that a significant part (98.36%) of the UV radiation energy is not absorbed, which gives a small value of $a_s \approx 0.11$ in comparison with such widely used pigments as ZnO ($E_g = 3.37$ eV at 300 K; Ref. 2), TiO_2 ($E_g = 3.05$ eV at 300 K; Ref. 3), and Zn_2TiO_4 ($E_g = 3.8$ eV at 300 K; Ref. 4). Also, because the irradiation dose will be significantly smaller for ZrO_2 powders compared with that for the aforementioned pigments at equal exploitation periods, the photostability must be high at UV irradiation of the sun for ZrO_2 pigments.

Zirconium dioxide powders generally have monoclinic lattice structure. Also, they are nonstoichiometric and unstable. Therefore, ZrO_2 pigments are easily colorized under the effect of light quanta or other type of ionizing radiation. This fact reduces diffuse reflectance and increases a_s during the exploitation period of the coatings on the base of these powders. Such coatings are used, for example, in spacecraft applications.

One of the well-known methods of improving the ZrO_2 stability is incorporation of doping elements with various cations. Their valency is lower in comparison with the valency of zirconium; it leads to an optimal decrease of cation–anion distance. In Refs. 5 and 6, ZrO_2 powders were stabilized with bivalent and trivalent cations (of strontium, calcium, and others). During incorporation of the aforementioned cations into zirconium dioxide lattice, anionic vacancies are formed, and they are potential electron color centers ($F-$ and F centers). Thereby, a negative effect based on the increase of anionic vacancies concentration occurs simultaneously with the positive effect of stabilizing and improving of photostability.

Enhancement of the stability of various pigments under the effects of various radiations is achieved via the monomolecular stratifying method. This method involves stratifying of a high-stable material on the grain surface of the pigment. This precludes the photolysis or radiolysis products outgoing from the reaction zone by means of creation of the barrier layer. Silicon dioxide is often used as the barrier layer.[7]

In the present work doping by strontium silicate was carried out for the purpose of examination of the aforementioned idea of stabilization of ZrO_2 by strontium cations. Silicon dioxide contained in strontium silicate may form a protective film on the grain surface of the ZrO_2. Such an effect of silicon dioxide was previously confirmed by the application of microcapsulation technology to ZrO_2 pigments.[8] The protective action of SiO_2 was also manifested by the example of ZnO pigment after its treatment with a potassium liquid glass (K_2SiO_3). Hence, photo- and radiation stability of the powders treated in such a way became greater.[9]

Experiment

Zirconium dioxide powder was of osobo khimichiski chistiy (OSCH) 9-2 purity grade with impurity content (mass %) of 2×10^{-5} for Fe, 7×10^{-6} for Cu, 2×10^{-6} for Ni, 2×10^{-6} for V, 1×10^{-6} for Co, 5×10^{-6} for Mn, 2×10^{-6} for Cr, 0.01 for sulfates, and 0.02 for chlorides. Purity of $SrSiO_3$ powder was not worse than 10^{-5} mass %.

Doping of ZrO_2 powders was carried out via mixing with $SrSiO_3$ powder in distilled water and baking at $T = 800$ K for 1 h, which led to the following reaction:

$$ZrO_2 + SrSiO_2 \rightarrow ZrSrO_3 + SiO_2$$

Concentrations of $SrSiO_3$ were 0, 1, 8, and 17.5 mass %. Powders were pressed under 20 MPa pressure into stainless steel cups. Reflective coatings based on the doped and undoped powders were produced by mixing the pigments with the binder 139-152 (polymethiladamantilsiloxane) in the proportion of 0.75:0.25 parts by weight. After that, several layers of coatings were deposited on the preprimed aluminum alloy substrate up to a thickness of 200–250 μm with the use of a paint pulverizer.

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Fabricated powders and coatings samples were placed on the sample stage of the Spektr-M ground simulation equipment, which imitates space environment conditions.[10] The diffuse reflectance spectra of the samples were measured before each session of irradiation (in situ). Samples were irradiated by unfiltered light of a high-pressure xenon lamp for which intensity in the UV part of spectra was measured via photocell and evaluated in equivalents of solar radiation (ESR) according to the method in Ref. 11. The durations of irradiation periods for powders were 10 and 18 h with $E_s' = 1.5$ ESR. Periods of irradiation for coatings were greater in comparison with that for the pigments at the same value of E_s'.

Results and Discussion

The effect of doping of ZrO_2 powders on their reflectance spectra is shown on Fig. 1. As we can see, the diffuse reflectance spectra are qualitatively the same. In the wavelength region of 330–335 nm, the drop of reflectance is observed that is typical for ZrO_2 powders. This drop is due to the intrinsic point defects (ions of Zr^{3+}, Ref. 12) and its value differs for powders with various concentration of strontium. The reflectance peak with a maximum at 420 nm is registered after the drop. The reflectance changes insufficiently from $\lambda \approx 515$ nm until $\lambda = 2100$ nm. But, the reflectance differs between samples in this region of spectra and it gives different values of a_s: 0.199, 0.183, 0.159, and 0.166 for strontium content 0, 1, 8, and 17.5 mass %, respectively. Thermal emittance ε for all the pigments and coatings was about 0.9 and during irradiation it had insufficiently changed (less than 5%).

The residual diffuse reflectance spectra (changes in reflectance) $\Delta\rho_\lambda$ were applied to analyze the effect of UV irradiation on reflectance of the samples. They were obtained as follows:

$$\Delta\rho(\lambda)[\%] = \rho_0(\lambda)[\%] - \rho_{\text{irr}}(\lambda)[\%]$$

where $\Delta\rho(\lambda)$ is the change in spectral reflectance, $\rho_0(\lambda)$ is the spectral reflectance of the unirradiated sample, and $\rho_{\text{irr}}(\lambda)$ is the spectral reflectance of the sample measured after its irradiation.

The reflectance decreases after irradiation in the whole spectral region. They are qualitatively the same after 10 and 18 h of EMR action. Figure 2 shows $\Delta\rho_\lambda$ spectra of the doped and undoped ZrO_2 powders after the UV irradiation for 18 h. As follows from this figure, the separate absorption bands are not manifested, and the absorption peaks are observed in the regions of 4.4–4.7 and 2.6–3.5 eV. Also, the narrow peak is resolved at 1.1 eV. Figure 3 shows the dependence of Δa_s from the dopant percentage. Changes in solar absorptance were obtained as follows:

$$\Delta a_s = a_{s0} - a_{s,\text{irr}}$$

where Δa_s is change in solar absorptance, a_{s0} is the solar absorptance of the unirradiated sample, and $a_{s,\text{irr}}$ is the solar absorptance of the irradiated sample.

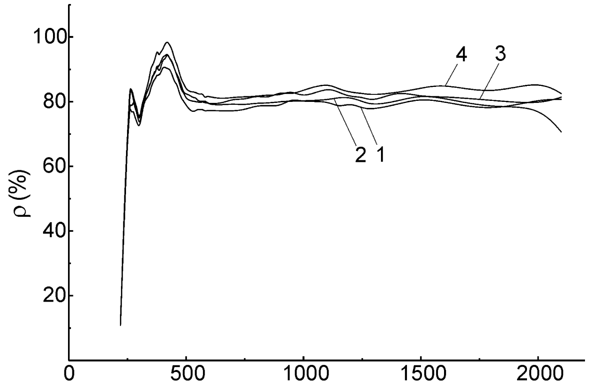

Fig. 1 Diffuse reflectance spectra of the ZrO_2 powders doped with $SrSiO_3$ (mass %): 0 (1), 1 (2), 8 (3), and 17.5 (4).

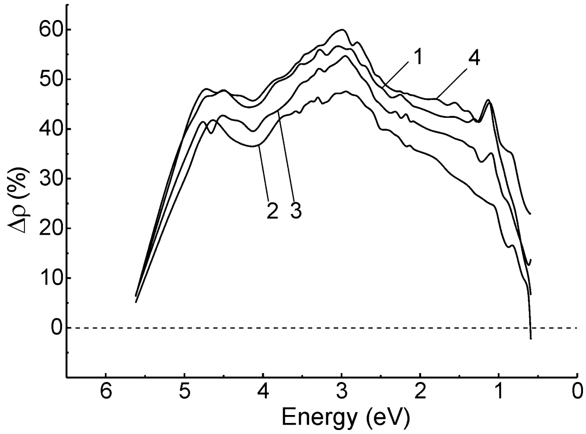

Fig. 2 Changes in spectral reflectance of the ZrO_2 powders doped with $SrSiO_3$ (mass %): 0 (1), 1 (2), 8 (3), and 17.5 (4), after UV irradiation (18 h with $E_s' = 1.5$ ESR).

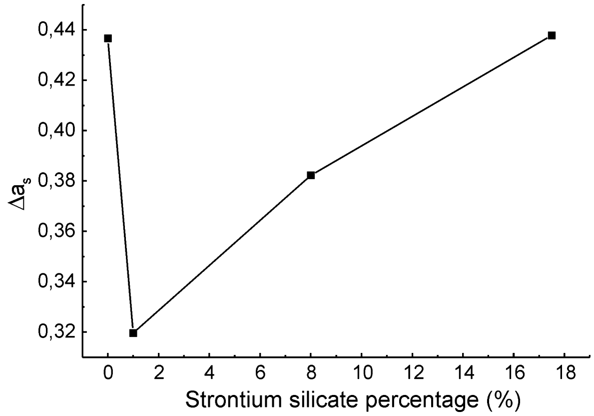

Fig. 3 Changes in a_s of ZrO_2 powders after the 18 h of UV radiation action with intensity of 1.5 ESR as a function of $SrSiO_3$ percentage (at temperature of 368 K).

It can be seen that the curve has a distinct minimum in the range 1–3% $SrSiO_3$. Zirconium dioxide powders have the greatest photostability in this range of doping level.

The two types of reflective coatings were fabricated on the base of the undoped powder (coating 1) and on the base of the powder doped by 1 mass % of $SrSiO_3$ (coating 2). Comparative investigations of their spectral reflectance and photostability were carried out. The coatings were irradiated at two temperature values. The first value was $T = 308$ K, which is close to room temperature (i.e., close to the temperature of the coating at the beginning of the life of the space vehicle), and the second one was $T = 368$ K (the temperature that is close to the operating temperature of the coating). The spectral reflectance was measured after exposure to UV with a period of 7–12 h. Technical malfunctions in the optical section of the installation occurred during the irradiation of coating 1. The depressurization of the vacuum chamber for rephotometry of the optical section was avoided in order not to disturb the integrity and propriety of the experiment. Therefore, the diffuse reflection spectra for coating 1 were recorded in the range 300–2100 nm in this experiment. The reflectance spectra of both coatings are shown in Fig. 4; it follows that the reflectance of the coatings is less in comparison with the pigments (Fig. 1); the reflectance of coating 1 is less in comparison with coating 2; the reflectance of coating 1 remains unchanged as the temperature increases, but the reflectance of coating 2 decreases; and the value of a_s for the coatings is greater in comparison with pigments and it increases with the temperature growth.

The changes in diffuse spectral reflectance of the coatings irradiated at temperatures of 308 and 368 K are shown in Figs. 5 and 6,

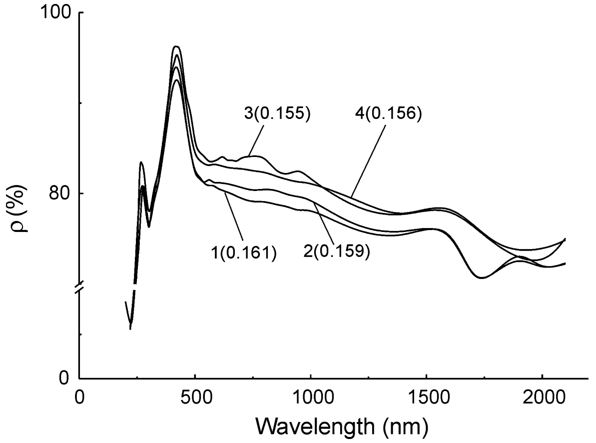

Fig. 4 Diffuse reflectance spectra of coatings 1 (curves 1 and 3) and 2 (curves 2 and 4) at temperature values of 308 K (curves 1 and 2) and 368 K (curves 3 and 4), respectively; values of solar absorptance are indicated in brackets.

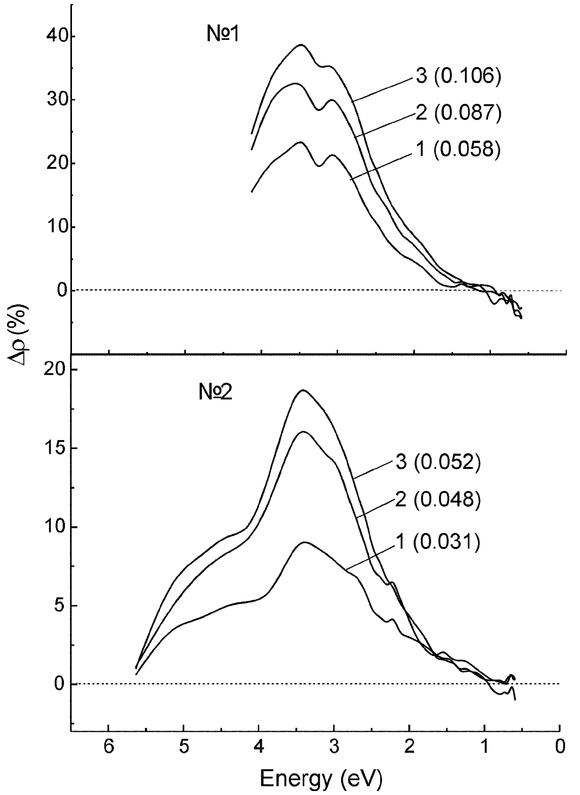

Fig. 5 Changes in the spectral reflectance of the coatings irradiated with UV at a temperature of 308 K for 8 (1), 16 (2), and 24 (3) h for coating 1 and 7 (1), 18 (2), and 27 (3) h for coating 2. Values of changes in a_s are indicated in parentheses.

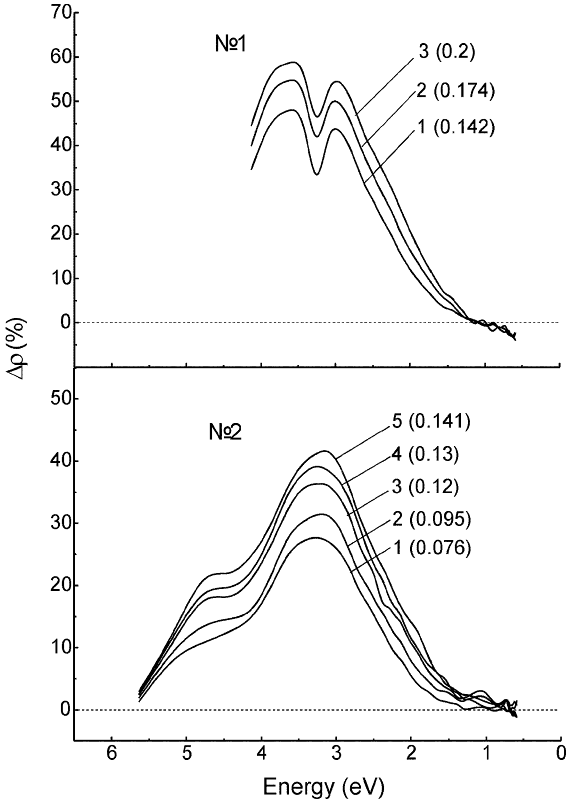

Fig. 6 Changes in the spectral reflectance of the coatings irradiated with UV at a temperature of 368 K for 11 (1), 18 (2), and 25 (3) h for coating 1 and 10 (1), 18 (2), 30 (3) h for coating 2. Values of changes in a_s are indicated in parentheses.

respectively. The spectra of both coatings consist of two regions: a high-energy part in the energy range 4–5 eV and a low-energy part in the energy range 3–4 eV. The shape of the spectra indicates that these parts are not individual absorption bands and include a few bands. It is notable that the ratio of $\Delta\rho$ values in maximums of high-energy and low-energy parts differs for coatings 1 and 2. For example, for coating 1 at 308 K, this ratio is 1.068, 1.066, and 1.078 for spectra 1, 2, and 3, respectively, whereas for coating 2 this ratio is 0.55, 0.51, and 0.49 for spectra 1, 2, and 3, respectively. Since, the absorption band of Zr^{3+} ions ($E_{abs} = 4.4$ eV) is located in the region of the high-energy maximum, and the absorption band of F centers ($E_{abs} = 3.78$ eV)[12,13] is located in the low-energy region, then the coating based on the doped pigment has a greater concentration of F centers compared to the concentration of Zr^{3+} ions. Such a ratio is due to the fact that the incorporation of Sr^{2+} ions into the lattice of ZrO_2 causes the formation of anionic vacancies, which, in turn, creates additional F centers during irradiation.

If we compare the absolute values of $\Delta\rho$ and the areas under the curves for the coatings and for the pigments (compare Figs. 2 and 5) at similar conditions of irradiation, we find that the coatings are more stable under the action of UV irradiation than the pigments. This fact is extraordinary, because in the case of coatings based on such widely used pigments as ZnO and TiO_2 the situation is reversed: the degradation of the optical properties of these coatings is higher than that of the pigments.[14,15] Moreover, the degradation of the coatings with an organic binder (polymethylsiloxane) is higher than the degradation of the coatings with an inorganic one (potassium liquid glass).[14] The higher degradation of the coatings (in the case of ZnO and TiO_2) can be explained by the transmission of the energy absorbed by the binder to the pigment, which causes an increase in the degradation. It is necessary to say that such a difference in the regularity of the photocolorizing processes for different coatings may be due to the fact that ZnO and TiO_2 are semiconductor compounds but ZrO_2 is a typical nonconductor. Although, on the other hand, it can be explained by the difference in stochiometric composition of these materials.[16,17] It is known[17] that ZrO_2 has a greater nonstochiometricity than ZnO or TiO_2, which facilitates the formation of color centers, especially at low doses of irradiation, when the dominating role plays the preradiative intrinsic point defects.

From the figures it follows that the coating based on the pigment doped by 1 mass % of $SrSiO_3$ has significantly greater photostability in comparison with the coating based on undoped pigment at both temperature values. For example, at $T = 308$ K, the values of Δa_s (after almost equal periods of irradiation) are 0.058 after 8 h of irradiation for coating 1 and 0.031 after 7 h of irradiation for coating 2; 0.106 after 24 h of irradiation for coating 1 and 0.052 after 27 h of irradiation for coating 2. The relative difference in the values of Δa_s for almost equal times of irradiation is about 50–60%. The

Table 1 Prediction of changes in Δa_s under the effect of space environment factors in LEO for coatings 1 and 2

T, K	Period, years	0.25	0.5	1	2	3	4	5	8	10
308	Coat. 1	0.34	0.367	0.391	0.413	0.425	0.433	0.439	0.451	0.457
	Coat. 2	0.216	0.239	0.261	0.282	0.294	0.302	0.309	0.322	0.328
368	Coat. 1	0.489	0.51	0.534	0.552	0.562	0.569	0.573	0.583	0.587
	Coat. 2	0.308	0.407	0.426	0.453	0.468	0.479	0.485	0.501	0.508

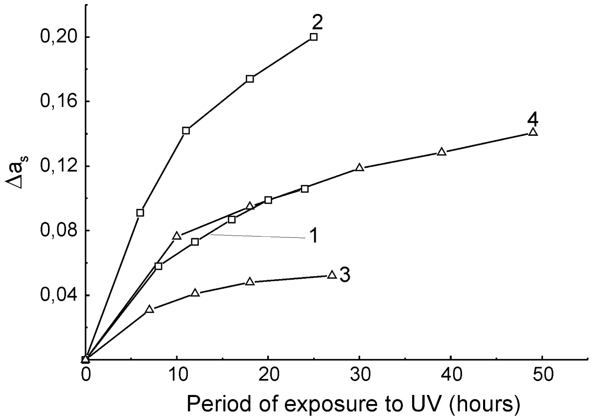

Fig. 7 Kinetics of changes in solar absorptance of coatings 1 (curve 1 and 2) and 2 (curves 3 and 4) after UV irradiation at temperatures of 308 K (curves 1 and 3) and 368 K (curves 2 and 4).

same regularity is observed for $T = 368$ K. The values of Δa_s are 0.142 after 11 h of irradiation for coating 1 and 0.0763 after 10 h of irradiation for coating 2; 0.2 after 25 h of irradiation for coating 1 and 0.1186 after 30 h of irradiation for coating 2. The relative difference of the values of Δa_s is about 32–45% at this temperature. Thus, the photostabiltity of the coating based on the pigment doped by 1 mass % of $SrSiO_3$ is about 30–60% higher in comparison with the coating based on the undoped pigment in the temperature range 308–368 K. Figure 7 shows the kinetics of the solar absorptance changes of these coatings irradiated at different temperatures. The long-term predictions are obtained for the degradation of a_s under the effect of EMR of the sun. The prediction was carried out with the assistance of a complex of mathematical models.[18,19] These models are a uniform pack of generic models and each one consists of two mathematic expressions. This complex allows for calculating the expected Δa_s values on the basis of one or two experimental kinetic curves at one value of test acceleration. Calculations may be carried out with a fixed or floating limiting value of Δa_s. Computations were carried out with the given limiting value of $\Delta a_s = 0.85$ for temperature values of 308 and 368 K independently and the following models were obtained. At $T = 308$ K, for coating 1,

$$\Delta a_s = 0.765 \cdot \{1 - 1/(1 + 2.84 \cdot [(1 + 0.1 \cdot t)^{0.0464} - 1])\}$$

and for coating 2,

$$\Delta a_s = 0.765 \cdot [1 - 1/(1 + 0.1 \cdot t)^{0.0617}]$$

At $T = 368$ K, for coating 1,

$$\Delta a_s = 0.765 \cdot \{1 - 1/(1 + 5.42 \cdot [(1 + 0.1 \cdot t)^{0.0525} - 1])\}$$

and for coating 2,

$$\Delta a_s = 0.765 \cdot [1 - 1/(1 + 0.1 \cdot t)^{0.12}]$$

The limiting value of Δa_s equal to 0.765 was obtained as a result of calculations for all the aforementioned models.

Table 1 shows the predicted values of Δa_s for coatings 1 and 2 in low-Earth-orbit (LEO) conditions.

It can be seen from the table that the degradation of the coating based on the undoped pigment is significantly higher in comparison with the coating based on the pigment doped with $SrSiO_3$ at both temperatures. The differences in stability of optical properties of these coatings are manifested in greater extent at $T = 308$ K than at $T = 368$ K.

Conclusions

The diffuse reflectance spectra, the integral solar absorptance factor, and their changes under the effect of the EMR that imitates solar spectra are investigated for ZrO_2 pigments doped by different concentrations of $SrSiO_3$. It was found that the optimal concentration of $SrSiO_3$ is 1 mass %.

The reflective coatings were fabricated on the base of the undoped powder and on the base of the powder doped by 1 mass % $SrSiO_3$. Comparative investigations of initial optical properties and photostability were carried out for these coatings. It was determined that the coating with the doped pigment has significantly greater photostability at the temperatures $T = 308$ and 368 K.

The specific feature was found for ZrO_2 pigments that the photostability of the pigment is lower than the photostability of the coating on its base in contrast to the other pigments with high diffuse reflectance (ZnO, TiO_2).

The calculations are made, the mathematical models of the degradation and the predictions of Δa_s are obtained for the aforementioned coating for a period of 15 years. These results may be used for altitudes of 600–800 km, during which the main damaging factor is the EMR of the sun.

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