PHOTOSTABILITY OF ORGANOSILICON LACQUER MODIFIED BY SiO_2 NANOPOWDERS – BINDER THERMALCONTROL COATINGS FOR SPACECRAFT

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ABSTRACT

The effect of modification of organosilicon varnish KO-859 by SiO_2 nanoparticles on the spectra and the solar absorptance of irradiated by quanta of the solar spectrum was investigated. It is established that the modification by nanoparticles leads to an increase in the radiation stability to irradiation of xenon arc lamps.

INTRODUCTION

Polymer lacquers and other polymeric materials are widely used in space technology as electrical insulating materials, various types of seals, bases of metal-organic compounds and binders of various coatings. Under the action of quanta of the solar spectrum and ionizing radiation, bonds in them break with form radicals, which lead to their destruction and in some cases to stitching.

The nanoparticles modification of inorganic compounds is sufficiently investigated and is used to increase their stability to the action of ionizing radiation [1-3]. The effect of quanta of various energies, including quanta of the UV region of the solar spectrum, has not been investigated. For organic compounds, in particular for varnishes, there is no information about the use of nanotechnology to improve photo- and radiation stability.

It was previously shown [4,5] that from many crystalline nanopowders of oxide compounds (ZrO_2, Al_2O_3, ZnO, TiO_2, Y_2O_3, CeO_2, $ZrO_2 \cdot Y_2O_3$, $Al_2O_3 \cdot CeO_2$), the SiO_2 powder differs in its amorphous state and a large specific surface. Such a difference is of particular importance for increasing the radiation stability of compounds that it modify.

This paper is devoted to the investigation the effect of SiO_2 nanoparticle modification on the photostability of the widely used silicone varnish KO-859.

EXPERIMENTAL

Silicon dioxide nanopowders were obtained from Plasmotherm OJSC [www.plasmotherm.ru] with a specific surface area of 150 m^2/g, an average grain size of 17 nm, and a purity of 99.8%. Samples for were prepared by dispersing the varnish in a solvent, followed by the addition of SiO_2 nanoparticles in an amount of 1 wt.%. The components were mixed in a magnetic stirrer under ultrasound impact.

The resulting solution was painted on a substrate of alloy AMG-6, dried at room temperature in air. The readiness of the samples was determined by solidification on metal substrates, which took place over 40 hours and indicated evaporation of acetone.

Samples were tested using the Space Environment Simulator in a vacuum $5x10^{-5}$ Pa at 300 K temperature. The irradiation was carried out by light quanta of Xenon arc lamp. The power of the lamp was 3 kW, the intensity of radiation in the UV region was 3.1 times higher than the intensity of the radiation from the supernumerary Sun: Es = 3.1 esi (equivalent of solar irradiation), 1 esi = 1390 W/cm^2.

The optical properties were estimated by recording spectral reflectance *in situ* by optical reflectance measurement system [6]. The change in spectra reflectance ($\Delta\rho_\lambda$) represents the radiation-induced absorption spectra, which is obtained by subtraction of the spectra after irradiation ($\rho_{\lambda f}$) from the spectra of the unirradiated samples ($\rho_{\lambda 0}$), while the transmission and the scattering under such conditions is not changed. The value solar absorptance of the samples was calculated by two experimental points in accordance with ASTM (E490 and E903-00a-96) [7, 8].

RESULTS AND DISCUSSION

In the initial state, it follows from the spectrum of reflection the varnish KO-859 (Fig.1) that the reflectance (ρ) in the visible region ranges from 50-60%. In the UV region, the reflectance decreases to about 15%. The decrease is determined by the edge of the main absorption of the oxidized substrate of an aluminum-magnesium alloy, on the surface of which there is always a film of aluminum and magnesium oxides. In the near IR region up to 2000 nm, ρ increases to 65%, then decreases with increasing wavelength, and at 2500 nm it is 45%. After irradiation, the reflectance decreases throughout the spectrum. But the greatest changes occur on the border of the ultraviolet and visible regions. With increasing exposure time, the change in the spectrum increases.

In the change in spectral reflectance (Fig.2), the absorption band in the UV and visible regions is recorded with a maximum at 420 nm. Its intensity reaches 30% after 5 hours of irradiation and increases to 37% with an increase in irradiation time to 30 hours. In the near-IR region, absorption bands appear at 820 and 1250 nm. These bands are less pronounced compared to the band at 420 nm. Their intensity is much lower - with a maximum exposure time of 30 hours, it is only 6-7%.

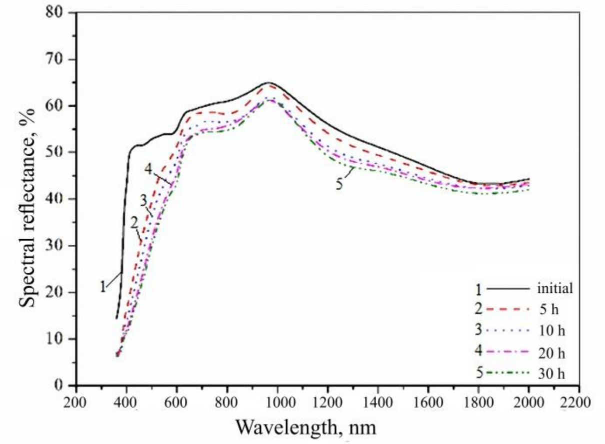


Fig. 1. The spectral reflectance of KO-859 varnish before and after irradiation with quanta of the solar spectrum for 5-30 hours with an intensity of 3.1 esi.

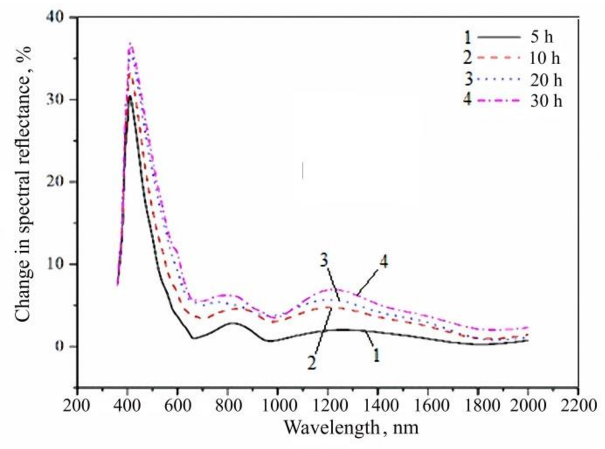


Fig. 2. Change in spectral reflectance of KO-859 varnish after irradiation with quanta of the solar spectrum for 5-30 hours with an intensity of 3.1 esi.

The reflectance of the modified varnish in the visible region is not significantly lower compared to the unmodified varnish (Fig.3). In the near-IR region from 1000 to 2100 nm, it is higher compared to unmodified varnish. In this part of the spectrum, its decrease with increasing wavelength is not observed. In this part of the spectrum, its decrease with increasing wavelength is not observed.

After irradiation with solar spectrum quanta, the reflectance decreases throughout the spectrum. But its greatest change occurs at the border of the UV-visible region. It should be noted a slight increase in the reflectance in the region from 600 to 1300 nm after the first period of irradiation for 5 hours.

In the change in spectral reflectance, the same absorption band at 420 nm is recorded as in the spectra of unmodified varnish. In the near-IR region, the $\Delta\rho$ values are significantly lower compared to the values in the spectra of unmodified varnish, at 5 hours exposure the values of $\Delta\rho$ are negative.

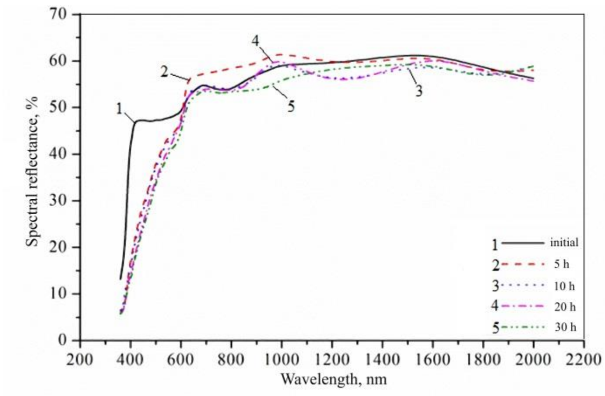


Fig. 3. The spectral reflectance of KO-859 varnish modified by SiO_2 nanoparticles before and after irradiation with quanta of the solar spectrum for 5-30 hours with an intensity of 3.1 esi.

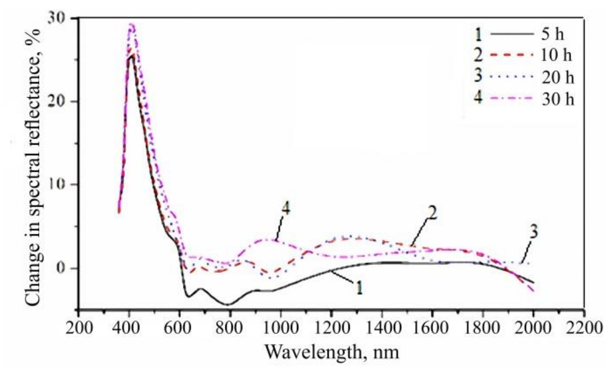


Fig. 4. Change in spectral reflectance of KO-859 varnish modified by SiO_2 nanoparticles after irradiation with quanta of the solar spectrum for 5-30 hours with an intensity of 3.1 esi.

KO-859 varnish is used as a binder for thermal control coatings of spacecraft. The temperature of a spacecraft is determined by the formula:

$T=k(a_s/\varepsilon)^{1/4}$,

where k - coefficient, ε - emissivity.

Emissivity is determined by the total volume of the thermal control coatings. Coatings based on pigments and binders, ε practically does not change under action of radiation from outer space [9]. It does not change when irradiated with oxide white powders (ZnO, TiO_2, ZrO_2, Zn_2TiO_4, etc.), which are pigments of thermal control coatings.

One should not expect its change when modifying varnishes with nanoparticles of low concentrations (≤ 5 wt.%). Therefore, the kinetics of changes in the solar absorptance Δa_s of thermal control coatings, in which lacquers are used as binders, determines the temperature of the spacecraft. Her research is of scientific and practical interest.

Figure 5 shows the dependences of $\Delta\alpha_s$ values on the irradiation time, calculated from the spectra $\Delta\rho_\lambda$ of unmodified and modified varnishes. From the figure it follows that the curve of the modified varnish is located significantly below the curve of the unmodified varnish.

With an increase in the irradiation time, the difference in the $\Delta\alpha_s$ values increases. For example, for t = 10 hours, it is 0.035 and 0.05 for modified and non-modified varnishes, respectively. The ratio of these values is equal to k = 1.43, i.e., the photostability of the modified varnish increases as many times as compared with the unmodified varnish. For t = 30 hours, the value of k = 1.65. Taking into account the value of E_s = 3.1 esi, we obtain for the time of irradiation with quanta of the solar spectrum for 93 hours in space the change in the solar absorptance of the modified varnish is 1.65 times smaller compared to the unmodified varnish.

To calculate the values of $\Delta\alpha_s$ for a longer irradiation time, approximation of the kinetic dependencies (Figure 6) was performed by the formula [10]:

$$\Delta a_s = k_1 \cdot \left(1 - \frac{1}{(1+k_2\cdot t)^{k_3}}\right) + k_4 \cdot \left(1 - \frac{1}{\exp(k_5\cdot t)}\right),$$

where:

- k_1 = 0.4147, k_2 = 0.039, k_3 = 0.1111, k_4 = 0.08177, k_5 = 0.2376 for unmodified varnish;
- k_1 = 0.15, k_2 = 0.0001555, k_3 = 11.99, k_4 = 0.05506, k_5= 0.1547 for varnish modified with nanoparticles.

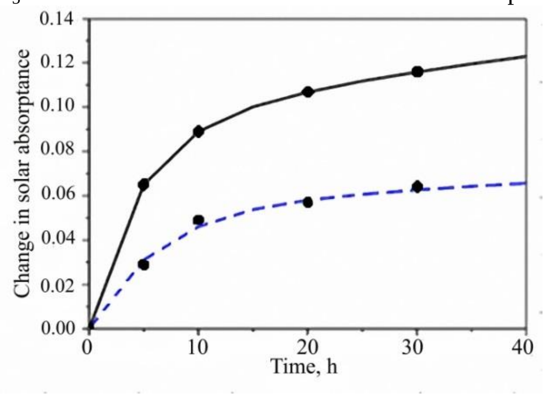
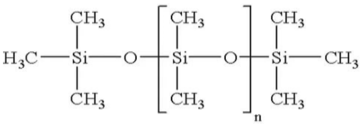


Fig.5. The experimental dependences of $\Delta\alpha_s$ under irradiation time at Es = 3.1 esi lacquer KO-859 unmodified (—) and modified by 1 wt.% SiO_2 nanoparticles (- - -).

Calculations performed for 5000 hours of irradiation show that $\Delta\alpha_s$ of unmodified varnish is 1.3 times greater than the value of varnished with nanoparticles. The structural formula of varnish KO-859 includes CH_3-Si and Si-O-Si bonds:



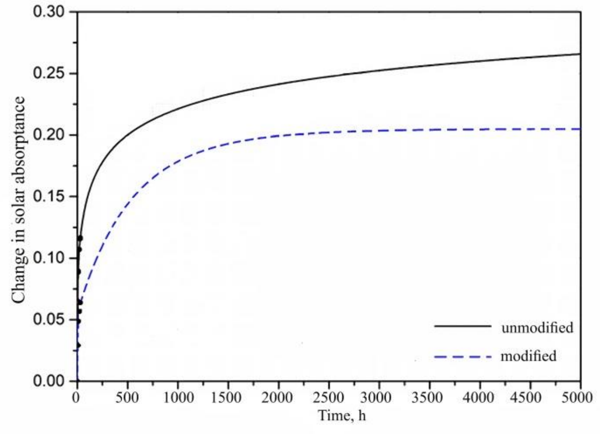
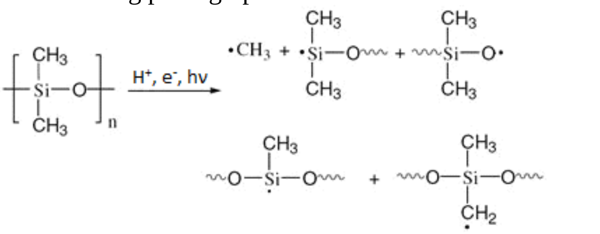


Fig.6 The calculated dependences of $\Delta\alpha_s$ under irradiation time at Es = 3.1 esi lacquer KO-859 unmodified (—) and modified by 1 wt.% SiO_2 nanoparticles (- - -).

Under quanta irradiation with an energy sufficient to break bonds, their photo destruction occurs with the formation of photographic materials. In the silicone lacquer, according to the studies performed [1, 11-13], the following photographic materials can be formed:



Polymer radicals are defects in the structure of varnish and absorb quanta of light, with the formation of absorption bands. Therefore, it can be assumed that the solar absorptance band in the visible region (Fig. 2, 4) is determined by the polymer radicals formed by irradiation.

In the spectra of the modified varnish, the intensity of the band is lower as compared to the unmodified varnish, which indicates a decrease in the concentration of polymer radicals and an increase in the photo-stability of the varnish. The increase in photo stability of varnish modified with SiO_2 nanoparticles may be due to the combination of polymer radicals with nanoparticle molecules and the formation of complexes.

CONCLUSION

In summary, the modification by 1 wt.% of SiO2 nanoparticles of the organosilicon lacquer KO-859 leads to a significant increase in the stability of its optical properties to the impact of the solar spectrum quanta. The efficiency of the modification determined by the ratio of the solar absorptance unmodified and modified lacquers, which is reaches values 1.3. The increase in photostability of the organosilicon lacquer modified by nanopowders result of oligomer chain ends crosslinking with inorganic complexes (nanoparticles) which occurs in three directions of volume. That reduces the generation of broken chain under the action of light quanta, which are often formed at the ends methyl, methoxy and polysiloxane group. Furthermore nanoparticles in polymer matrices can be the drain of an electron and hole, as well as the place of scattering polarons which are formed under the influence of radiation and localized on free radicals. Modification by nanoparticles can be used to extended service lifetime of thermal control coatings of space vehicles.

ACKNOWLEDGMENT
This work was financially supported by the Federal Target Program of the Ministry of Education and Science of the Russian Federation, project No. 14.574.21.0176 and federal target program research and development of the Russian Federation Ministry of Education and Science No. 1.875.201.2017/8.9, 3.5512.2017/БЧ is greatly appreciated.

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