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EFFECT OF TITANIUM DIOXIDE ON THE SELF-CLEANING PROPERTIES OF PAINTS FOR ETICS

WPŁYW DWUTLENKU TYTANU
NA WŁAŚCIWOŚCI SAMOCZYSZCZĄCE FARB
DO BEZSPOINOWYCH SYSTEMÓW OCIEPLEŃ

A b s t r a c t

The influence of a nano-particle addition on the self-cleaning properties of exterior paints for External Thermal Insulation Composite Systems is analyzed. The effect of UV radiation on the color change of paints containing normal pigments and the photo-catalyst titanium dioxide is laboratory tested. To evaluate self-cleaning properties of the paints and their color change due to accelerated weathering processes spectro-photometric tests were performed.

Keywords: *External Thermal Insulation Composite Systems, facade paints, nanotechnology, photocatalyst titanium dioxide*

S t r e s z c z e n i e

W artykule przeanalizowano wpływ nano-dodatku na właściwości samoczyszczące farb elewacyjnych stosowanych w systemach ETICS. Badano zmiany barwy powłok zawierających zwykłe pigmente i foto-katalityczny dwutlenek tytanu wskutek działania promieniowania UV. Samoczyszczące właściwości zabrudzonych powierzchni farb i zmiany ich barwy podczas przyśpieszonego procesu starzenia zbadano ilościowo za pomocą techniki spektrofotometrycznej.

Słowa kluczowe: *Bezspoinowe Systemy Ociepleń, farby do elewacji, nanotechnologia, fotokatalityczny dwutlenek tytanu*

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1. Introduction

Nanotechnology is a promising field of research, allowing for significant improvements and/or modifications of physical and service properties of many materials used in building structures. Examples of such products, obtained by addition of nano-particles of silver, copper and/or titanium dioxide are: external renders, key coats, finishing coats, plaster-boards, polymer based or gypsum finishing systems, decorative renders, paints, grouts, self-cleaning glass, air conditioners, etc., see e.g. [1–3].

Different amounts of some additives, including pigments and nano-particles, are used in paints in order to obtain the required color and/or self-cleaning properties. The purpose of this study is to examine self-cleaning properties of silicone façade paints, containing different amounts of photo-catalyst titanium dioxide. The specimens of ETICS system were tested. First accelerated weathering of the paints with the UV irradiation and water vapor condensation was applied in the fluorescent UV device ATLAS UV2000. This is a screening device for reproducible, accelerated weathering testing of the sun's damaging effects on various coatings. Then the color tests were performed by means of a spectro-photometer Konica Minolta CM-2500d, in order to assess the self-cleaning properties and resistance of the surface to the UV irradiation.

2. Materials

The specimens of External Thermal Insulation Composite System with the dimensions 20 cm × 5 cm, were made in the laboratory.

The tested paints were prepared on a basis of silicone dispersion. The composition of different types of paints varied in content from titanium white, photo-catalyst titanium dioxide UVLP 7500, organic pigment powder (pink or yellow). The specimen symbols and the contents of chemical components are given in Table 1.

Table 1
Symbol of specimen and contents of each chemical components

| Specimen symbol | Titanium White [%] | UVLP 7500 [%] | Organic Pigment [%] |
|-----------------|--------------------|---------------|---------------------|
| S1 | 6.3 | – | 0.2 (pink) |
| S2 | 6.3 | 0.5 | 0.2 (pink) |
| S3 | 6.3 | 0.5 | – |
| S4 | 6.3 | – | 0.2 (yellow) |
| S5 | 6.3 | – | – |
| S6 | 6.3 | 0.5 | 0.2 (yellow) |
| S7 | – | – | – |
| 5 | – | 5 | – |
| 6 | – | 10 | – |
| 7 | – | 15 | – |

The paint components were weighed and mixed. Then, the paints were applied on the surface of base coat of ETICS and then stored for at least 14 days at $(23\pm2)^\circ\text{C}$ and $(50\pm5)\%$ RH. The UVLP 7500 nano-powder content of 0.5% is a standard quantity in façade paints produced in the factory. This powder contains no addition of pigments and it is a pure titanium dioxide (TiO_2). The UVLP 7500 is a photo-catalyst designed to improve paint durability against UV radiation. It is also suitable for eliminating unwanted odors such as vehicle emissions; for air purification from organic compounds such as nitrogen oxides, sulfoxides and chlorinated hydrocarbons [4]. The photo-catalyst titanium dioxide also eliminates soiling or contamination on the façade surfaces from substances like e.g. soot.

The next step of specimen preparation was the application of different types of dirt, in order to check self-cleaning properties of the tested paints. The upper part of the specimens remained clean and was used to test the effects of solar irradiation and water vapor condensation. The rest of the specimens' surface were covered with three types of contaminants, most commonly encountered on real building façades.

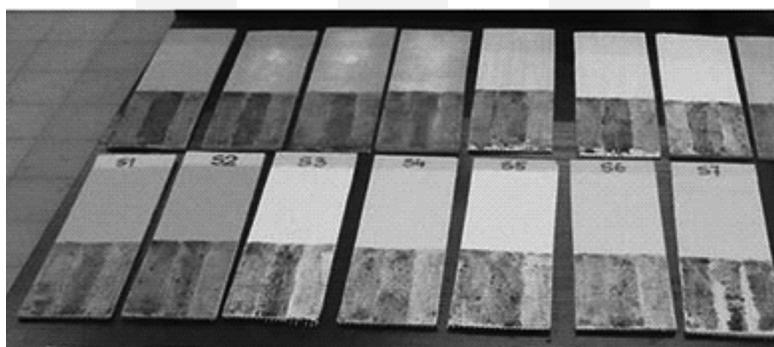


Fig. 1. The test samples before application of the UV radiation

The three types of contaminant were applied by means of painting with 10% 'dirt solutions' in distilled water. One sixth of each sample surface was covered with the carbon soot contamination, one sixth with the carbon ash contamination, and one sixth with the dust contamination. The dust was collected from the facades and windows of the university buildings, at a height of about 3 meters from the ground level. This is probably the kind of contamination which the facades of buildings are mostly exposed to.

3. Test methods

For testing the radiation resistance and self-cleaning properties, the fluorescent UV devices ATLAS UV2000 were used. The heated reservoir below the test chamber produced water vapor that was rising to the upper chamber, where specimens were exposed to the UV irradiation and uniform wetting at 100% RH. One test cycle consisted of irradiation of the samples by the fluorescent UV lamp and then condensation of water vapor. The samples were tested according to the Polish standard PN-C-81913:1998 [5] after the 50 cycles, consisting of the following phases:

- 4 hour UV-A (340 nm) irradiation of the intensity 0.65 W/m^2 at a temperature of $60\pm2^\circ\text{C}$,
- 4 hour water vapor condensation at a temperature of $40\pm2^\circ\text{C}$.

Hence, the total testing time in the chamber was equal to 400 hours. Next macroscopic color of the samples' surface was evaluated by means of the spectrophotometer Konica Minolta CM-2500d.

Color space CIELab has been normalized by CIE (the International Commission on Illumination (also known as the CIE from its French name, the Commission Internationale de l'Eclairage) is devoted to worldwide cooperation and the exchange of information in all fields of science and art concerning light and lighting, color and vision, photobiology and image technology. The color space defined by the CIE is based on one channel for Luminance (lightness) (L) and two color channels (a and b) [5]. A problem related to a XYZ color system, is that colorimetric distances between the individual colors do not correspond to perceived color differences. For example the difference between green and greenish-yellow is relatively large, whereas the distance distinguishing blue and red is quite small. The CIE solved this problem in 1976 with the development of the three-dimensional Lab color space (or CIELab color space). In this model, the color differences which are perceived correspond to the distances measured calorimetrically. The 'a axis' extends from green ($-a$) to red ($+a$) and the 'b axis' from blue ($-b$) to yellow ($+b$). The brightness (L) increases from the bottom to the top of the three-dimensional model. This color space is currently the most popular method for describing the color and forms a basis of modern color management systems [6]. In the CIELab color space, the color difference can be expressed as a single numerical value, ΔE , which indicates the size of the color difference, but not in what way the colors are different. ΔE is defined by the following equation [6]:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

and is the simple Euclidean distance between two points in three-dimensional space.

It can be assumed that the color difference noted by the standard observer can be described as follows:

- $0 < \Delta E < 1$ – the difference cannot be noticed,
- $1 < \Delta E < 2$ – the difference can be noted only by an experienced observer,
- $2 < \Delta E < 3.5$ – the difference can be also noted by an inexperienced observer,
- $3.5 < \Delta E < 5$ – a clear difference of color can be noted,
- $5 < \Delta E$ – the impression of two different colors is noted.

In the research a three-dimensional classification was used, based on the relative spectral power distribution of the CIE standard illuminant D_{65} and the 10° supplementary standard observer. The symbol D_{65} suggests that the related color temperature should be 6500 K, while in reality it is closer to 6504 K [7].

Our perception and interpretation of color are highly subjective. Color measurement is the determination of the characteristics of electromagnetic radiation entering an eye. It is difficult to describe objectively any particular color to someone without the same type of standards. The solution is application of a measuring instrument that explicitly identifies the color. Spectrophotometer is an instrument that differentiates any given color from all the others and assigns it a numeric value.

4. Results

The three color components were measured in the three points on the surface of every specimen and the results were averaged. The samples were tested with the spectrophotometer, before and after 50 cycles of aging. Results for clean paints are shown in Table 2.

Table 2
The difference in color and lightness after exposition to the UV radiation - clean paints

| Symbol of specimen | The difference in color ΔE after the UV cycles | The difference in lightness ΔL after the UV cycles | Color of paint |
|--------------------|--|--|----------------|
| S1 | 1.58 | 0.71 | pink |
| S2* | 2.39 | 0.88 | pink |
| S3* | 1.18 | -0.92 | white |
| S4 | 1.79 | -0.45 | yellow |
| S5 | 1.04 | -0.84 | white |
| S6* | 1.02 | -0.81 | yellow |
| S7 | 2.46 | -1.88 | transparent |
| 5* | 2.82 | 2.72 | white |
| 6* | 2.29 | 1.83 | white |
| 7* | 2.35 | 1.64 | white |

* The paint contains the nano-powder

The results obtained for sample S7 indicate an important effect of the UV irradiation on the color change for the pure silicone dispersion without any pigments, what influenced also the other results. To show character of the change, another parameter showing the difference in lightness/darkness value ΔL (positive ΔL means lighter, negative – darker colour) was used. The difference ΔL is defined by the following equation:

$$\Delta L = L_1 - L_2 \quad (2)$$

where:

L_1 – lightness sample after aging UV radiation,

L_2 – lightness sample before aging UV radiation.

After the UV irradiation, the surface painted with pure silicone dispersion (sample S7) darkened. Application of larger amounts of the photocatalyst titanium dioxide caused significant brightening of the surface. This may mean destruction of the silicone dispersion in presence of the UVLP 7500. The 0.5% admixture of nano-powder had not a significant influence on the results obtained. For the color change both the pigment and the dispersion were responsible.

The color measurement results in the case of surfaces soiled with different pollutants are shown in Fig. 2. The results show that the color aging depends on the type of pollution.

The results clearly indicate that admixture of the photo-catalyst titanium dioxide to the paints in the amount of 0.5% does not activate the self-cleaning properties. In this case

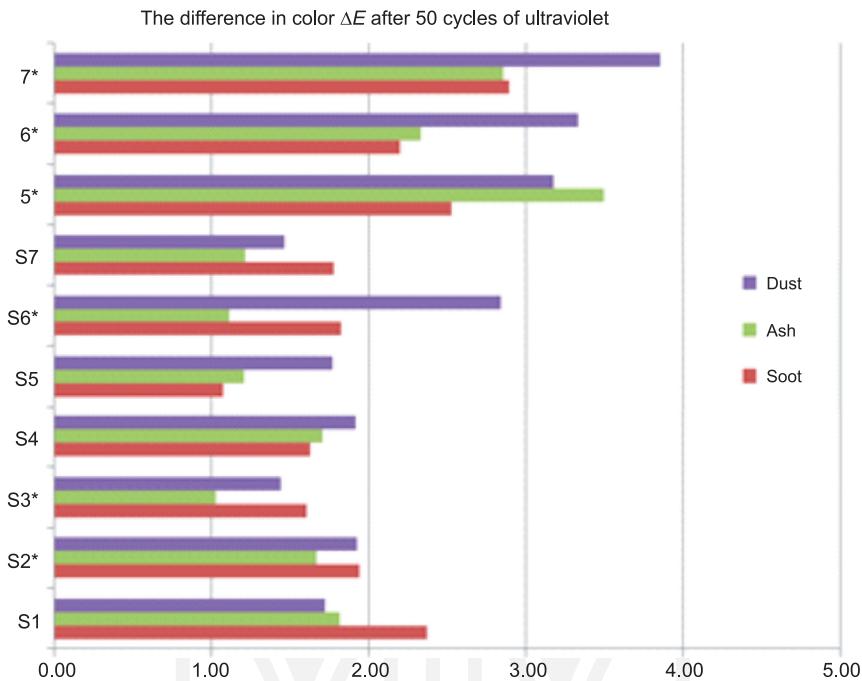


Fig. 2. The differences in color of polluted paints after the UV irradiation

the nano-powder is too dispersed within volume of the paint. A noticeable self-cleaning effect can be obtained only after adding several times larger amount of the UVLP 7500 (Fig. 3).

Figure 3 indicates, that obtaining self-cleaning properties of the façade surface is possible by adding the photo-catalyst titanium dioxide to the silicone paint. It is important to properly select the paint composition. The nano-powder applied in too small amounts does not work,

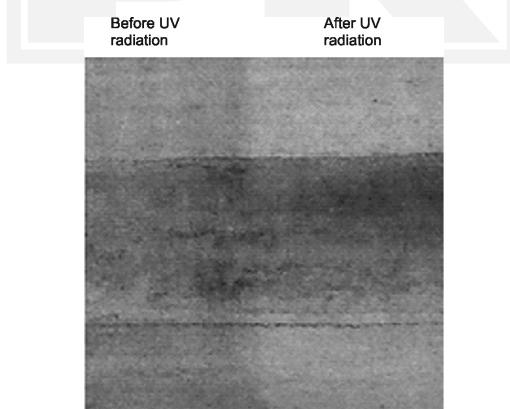


Fig. 3. Photo of the sample No 6 with 10% UVLP 7500, before and after exposition to the UV radiation

while the amounts exceeding a certain level can destroy the paint organic binder. Obtaining the self-cleaning paints may depend on other factors as well. For example the sample S7 showed a hydrophobic (water resistant) behavior and it was even very difficult to apply

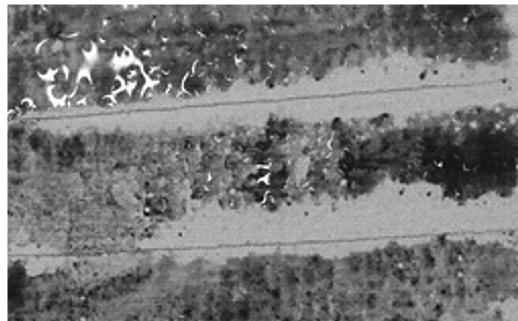


Fig. 4. Photo of sample No S7, the polluted surface of the clean silicon dispersion

soiling on its surface (Fig. 4). During pollutant painting, drops of water and soiling did not adhere to the surface, but flowed down freely. The sample showed a greater resistance to attempts of soiling than the dispersions with pigments.

5. Conclusions

There is lack of standardized methods for testing the self-cleaning properties for facade paints. The surface of the tested silicone paints, without and with different additions of the nano-powder, after weathering by means of UV irradiation and water vapor condensation, exhibited visible aging effects for the all paints.

The studies performed revealed that the properties of ‘self-cleaning surface’ have been measured for the paints containing at least 5% of the photo-catalyst titanium dioxide, and were clearly visible for its amount in the paint of at least 10% by weight.

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