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PHOTODEGRADATION OF MODERN PAINTINGS via TiO_2-INDUCED PHOTOCATALYTIC PROCESS

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Rezumat. *Această lucrare explorează potențialul nanoparticulelor de dioxid de titan (TiO_2) în procesul de conservare și/sau restaurare ale unor artefacte, punând în evidență natura lor fotocatalitică, care contribuie adesea la degradarea suprafețelor pictate. Radiația luminoasă UV afectează proprietățile fotocatalitice ale TiO_2, permițându-i să descompună contaminanții organici de pe suprafața picturilor, și uneori conduc la modificări de culoare ale straturilor pictate. Sunt folosite mai multe tehnici pentru a evalua eficacitatea nanoparticulelor de TiO_2: Microscopia optică (MO), Microscopie electronică cu baleiaj (SEM), Microscopie de forță atomică (AFM), Spectrofotometrie UV-Vis, FTR și Raman, precum și colorimetria și glossmetria. Radicalii generați de interacțiunea dintre TiO_2 și lumina UV pot descompune pigmentul prezent în vopsea, conducând la cretare, decolorare și pierderea integrității operei de artă în timp. Este discutat cazul pigmentului 588 comercial.*

Abstract. *This paper explores the potential of titanium dioxide (TiO_2) nanoparticles in the conservation and/or restoration process of some artifacts, highlighting their photocatalytic nature, which often contributes to the degradation of painted surfaces. UV light radiation affects the photocatalytic properties of TiO_2, allowing it to break down organic contaminants on the surface of paintings, and sometimes lead to color changes in the painted layers. Several techniques are used to evaluate the efficacy of TiO_2 nanoparticles: Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), UV-Vis Spectrophotometry, FTR and Raman, as well as colorimetry and glossmetry. The radicals generated by the interaction between TiO_2 and UV light can break down the pigment present in the paint, leading to coating, discoloration, and loss of the integrity of the artwork over time. The case of commercial pigment 588 is discussed.*

Keywords: painting; pigments; TiO2; UV-ageing; glossmetry.

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1. Introduction

Artifacts and monuments belonging to cultural heritage are susceptible to various forms of degradation due to biological, physical and chemical agents, which affect not only their structural integrity but also their aesthetic value, including changes in colour and loss of mechanical strength, for this reason their conservation is a delicate and continuous challenge [1-3]. To address these threats, conservation and preservation treatments have evolved significantly.

Thus, the use of consolidants - substances that penetrate the material and strengthen it (resins, polymers or gels), make the artefact more durable, leaving its surface appearance largely unaffected. Modern conservation techniques focus on gentler methods, such as the use of nanomaterials and nanotechnology without affecting the original material [4].

Titanium white (titanium dioxide) is commonly used as a white pigment in many works of art, but over time, its photocatalytic properties can cause degradation when exposed to UV light. This degradation is particularly slow, which is why there are not many documented cases yet, but it is expected to become more noticeable as these artworks age [5-10].

UV light accelerates the process because titanium dioxide can act as a photocatalyst, breaking down surrounding materials when exposed to light, leading to chemical changes that can affect the surface of the painting, such as discoloration or loss of pigment integrity [11]. Photocatalytic behavior under exposure to UV light radiation could lead to undesirable consequences for artworks over long periods. The practical weathering of a pigmented system is a result of at least two separate processes (a) the direct homogeneous photochemical oxidation of the organic medium and (b) the heterogeneous photo-catalytic oxidation caused by the titanium dioxide pigment [12].

The photochemical activity of TiO_2 depends on its form: rutile and anatase. The band gap for rutile TiO_2 is 3 eV, and for anatase TiO_2 it is 3.2 eV. The band gap is a key factor in determining the energy required to excite electrons in the material. TiO2 also exists as brucite, but this form is not very stable and cannot be used. When TiO_2 absorbs UV light, it generates free electron-hole pairs. These are high-energy particles that can travel to the surface of the TiO_2 crystal. The free electrons and holes on the TiO_2 surface react with oxygen and water in the environment, producing reactive oxygen species such as hydroperoxyl radicals (HO_2) and hydroxyl (OH). Hydroxyl radicals are particularly reactive and can cause chemical breakdown in organic materials, such as the binder in a painting, leading to a loss of cohesion and eventual decomposition of the surface. This latter effect is known in the art as chalking. This results in a powdery or chalk-like texture [13].

To investigate these issues, samples prepared with materials and coatings similar to the original artifacts are an essential step in simulating the degradation process. This study helps to understand how TiO_2 NPs would function under controlled conditions, providing valuable information on their potential hazard in the preservation of original painted surfaces. Accelerated aging tests can cause natural degradation of pigments, and the evidence of degradation effects is highlighted by microscopic techniques, FTIR, Raman and UV-Vis spectroscopy and last but not least by colorimetry and glossmetry.

2. Materials and methods

2.1. Materials

Preparation of the Painting Layer on the Stone and Wooden Samples

To replicate the original material, wooden samples of native Sycamore (2.5 x 2.5 x 2.5 cm) were prepared in the lab. and coated with a mixture of animal glue and Calcite. The samples were then painted with pasta (588) using Daler Rowney Inc.'s (naphthol red and diarylamide yellow). The pigment was blended and applied over a white preparatory layer. The painted samples were left to dry for seven days (Fig. 1).

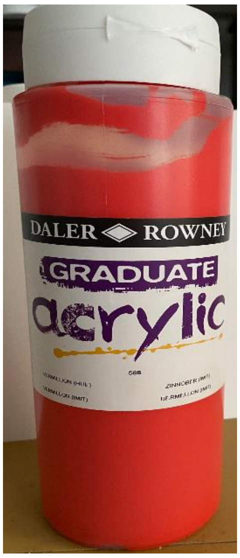


Figure 1. The painting paste 588

2.2 Accelerated artificial aging processes

The painted specimens were exposed to three accelerated artificial aging processes to evaluate the chemical stability and physical durability of the materials. Light-accelerated aging was performed at a distance of 20 cm from a mercury-ARC lamp of 375 W/cm^2.

2.3 Characterization techniques

The optical microscopy was performed with a Novex trinocular microscope (at different magnifications). Also, the optical microscopy has been recorded by a Primo Star ZEISS optical microscope that offers the possibility to investigate the samples in transmitted light at a magnification between 4X and 100X. The equipment had attached a digital video camera (Axiocam 105) which, by the microscope software, allowed real-time data acquisition. The obtained images could easily be converted from 2D in 3D format through its software for a better viewing.

The Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) results were obtained by a *SU*-70 *(Hitachi*, Japan) microscope, used for characterization of micro- and nanomaterials qualitative and quantitative analysis of samples and composition of the structure for a sample surface, respectively.

UV-Vis spectrophotometry has been measured with a M400 Carl Zeiss Jena UV spectrophotometer with a 1 nm slit width, 1 nm step size, 0.3 nm/s average scan rate, deuterium lamp, double beam, microprocessor, and quartz cell was used to measure the aqueous solution absorbance for each sample at 22°C.

Fourier transformed infrared spectroscopy (ATR-FTIR) has been recorded with a Vertex 80 spectrometer (Bruker Optik GMBH, Germania) in the range of 4000–400 cm^{-1}, equipped with DRIFT accessory.

Raman spectra have been recorded with a FirstGuard Raman apparatus, BaySpec with two wavelengths (1064 and 785 nm).

Color measurements have been recorded with a CM-2600d spectrophotometer (KONICA MINOLTA) (Japan) under a D65 light source and an observer angle of 10°. The measured color value is interpreted by the CIE L*a*b* color space. This color space is based on three axes: L* (Lightness): Represents the lightness of the color, with values from 0 (black) to 100 (white), a*: Represents the green to red axis, with negative values indicating green and positive values indicating red, b*: Represents the blue to yellow axis, with negative values indicating blue and positive values indicating yellow, and Color Difference (ΔE*): The color change between the original and altered sample is evaluated using the ΔE* formula:

$$\Delta E^* = (L^{*2} + a^{*2} + b^{*2})^{1/2} \qquad (1)$$

This value represents the distance between the original and altered colors in the color space. The larger the ΔE*, the greater the color change.

The Sheen **Glossmeter** was used to measure the gloss of the samples at three different angles: 20°, 60°, and 85°. The gloss value reflects how shiny or matte a surface is, with a scale from 0 to 100 Gloss Units (GU). The 60° measurement is primarily used to determine the gloss.

3. Results and discussion

Titanium white pigments, introduced in the 1920s, are known for their photocatalytic properties, which can lead to several degradation phenomena in paint films, such as chalking and degradation of colored pigments. This degradation occurs when UV excitation of TiO_2 leads to the formation of reactive radicals at the pigment surface, which can attack the surrounding materials, causing degradation, Scheme 1 [14-18].

$TiO_2 \rightarrow h^+ + e^-$ (2)
$h_{VB}^+ + H_2O\ (OH^-) \rightarrow OH^\bullet$ (3)
$e_{CB}^- + O_2 \rightarrow O_2^{\bullet -}$ (4)
$h_{VB}^+ + OH- \rightarrow OH^\bullet$ (5)
$h_{VB}^+ + O_2^{\bullet\,-} \rightarrow HO_2^-$ (6)
$(OH^\bullet, HO_2^-, O_2^{\bullet -})$ + organic compounds → degraded compunds $^\bullet + CO_2 + H_2O$ (7)

Scheme 1. The processes of the photocatalysis with TiO_2

For evaluation of the efficacity of TiO2 as photocatalysts in 588 painting pasta, the UV-Vis spectra have been measured, [19], Figure 2. From the UV-Vis absorption spectra it can be seen that the only band of titanium white left intact at the same wavelength, while the bands belonging to the constituent pigments of the 588-painting paste are completely modified after only 41 hours of irradiation. The peaks specific to this painting paste decrease significantly and undergo bathochromic changes and in the area of 700-1000 nm new bands of very high intensity are recorded.

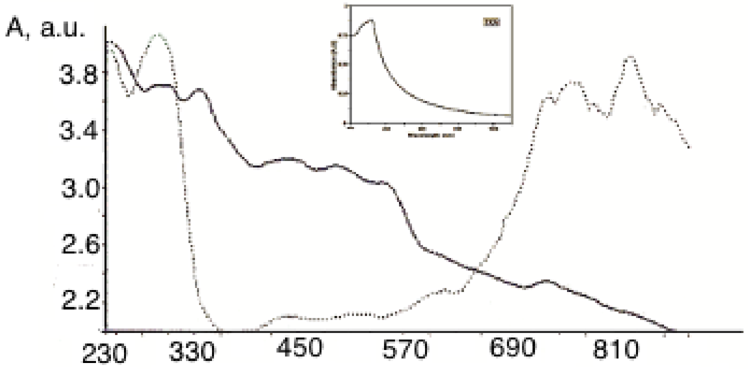


Figure 2. UV-Vis spectra of 588 painting paste: non-irradiated with UV light (___) and irradiated 41 h with UV light (…..) (TiO_2 spectrum inset)

FTIR spectroscopy was used to analyze the color change in the pigment, helping to detect changes in the chemical composition and surface structure due to aging and various treatments [20] (Fig. 3). The FT-IR spectrum of the fresh green paint layer (reference sample) showed key characteristic peaks (Table 1).

Table 1. Key characteristic peaks of the FT-IR spectrum of the fresh green paint layer

Peak, cm^{-1}	Assignment
1459 cm^{-1}	Calcium carbonate (CO_3^{2-})
878 and 876 cm^{-1}	O-C-O bending
1049 cm^{-1}	C-C and C-O

FT-IR analysis provided valuable insights into the effects of accelerated aging and treatment materials on the investigated pigments [21]. TiO_2 NPs in pigment were not the most effective at preserving this pigment (Naphthol Red) present in 588 painting paste, leading to significant color change and maintaining the pigment's chemical integrity. After accelerated aging, with and without the addition of TiO_2 NPs dispersed in pigment, the FT-IR spectrum showed the characteristic vibrational modes at 1043, 820, 750, 570, and 523 cm^{-1}. (Figures 3, 4)

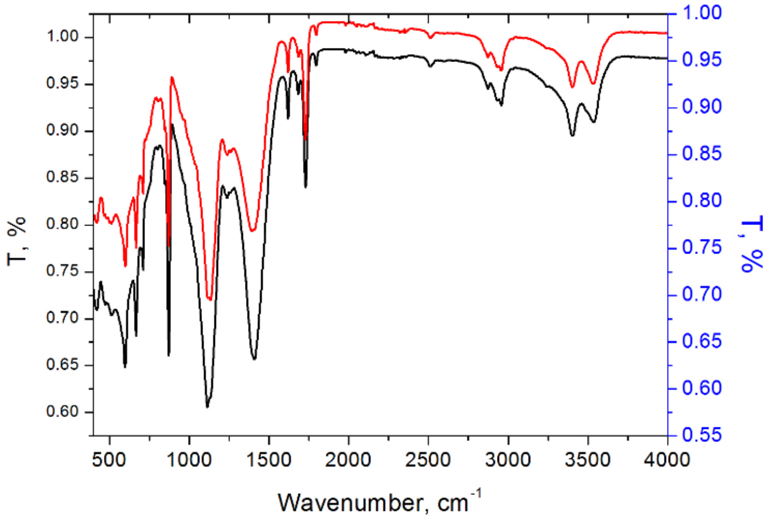


Figure 3. FTIR of 588+TiO_2 layer: non-iradiated (black) and irradiated 41 h (red)

The Raman spectra of 588 pigment were obtained before and after aging, with and without the addition of TiO_2 NPs dispersed [22]. Some specific peaks at 712, 750, 1055, 1092, 1365, and 1491 cm^{-1}, have been obtained as in Table 2.

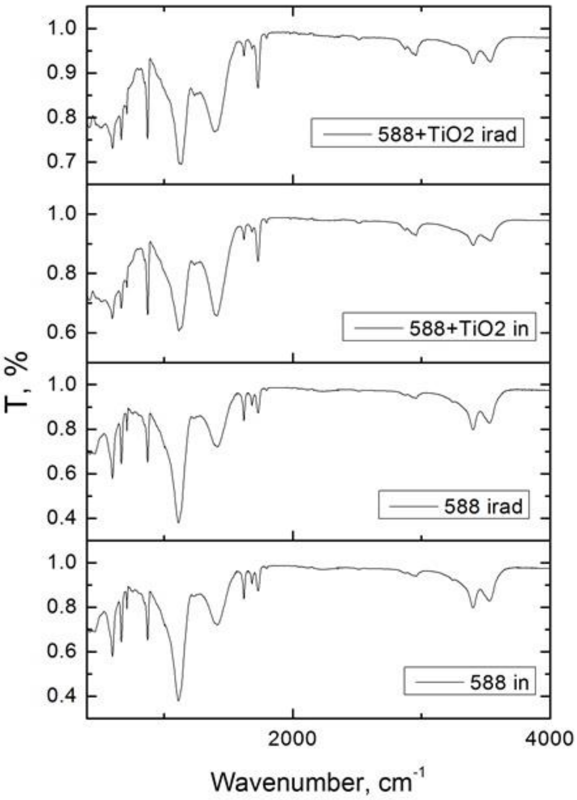


Figure 4. FTIR spectra of all cases investigated (see legends)

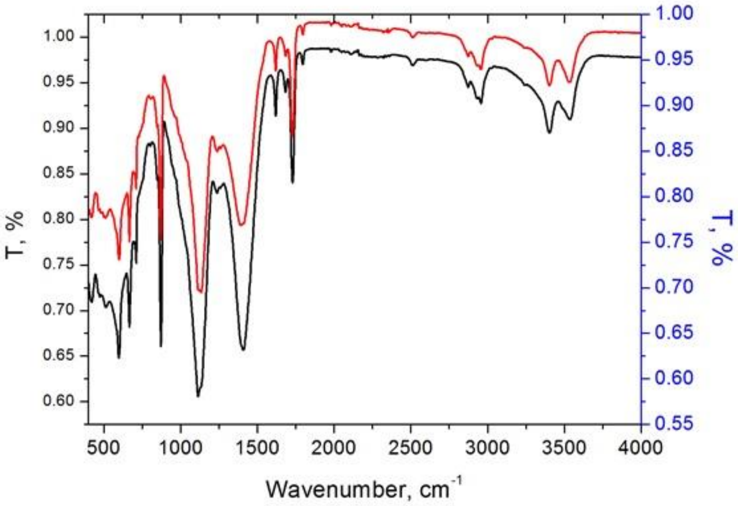


Figure 5. Raman spectra of 588+TiO_2 before (black) and after irradiation (red)

Table 2. Raman specific spectra at various wave lengths

Peak, cm^{-1}	Assignment
1492 cm^{-1}	C–C stretching vibration of the ring.
1367 cm^{-1}	in-plane N–phenyl stretching vibration.
1096 cm^{-1}	C–C stretching vibration
750 cm^{-1}	Aromatic C–H vibration
715 cm^{-1}	Ring-breathing and out-of-plane phenyl–H bending vibrations.

Raman spectroscopy revealed that the TiO_2 NPs dispersed in painting paste 588 had the most significant effect on the change of naphthol red, particularly in preserving the vibrational intensity of key characteristic peaks. This clearly outlines the stages of photocatalytic degradation in paint films due to the presence of titanium white pigments, specifically focusing on how titanium dioxide (TiO_2) contributes to the breakdown of this pigment.

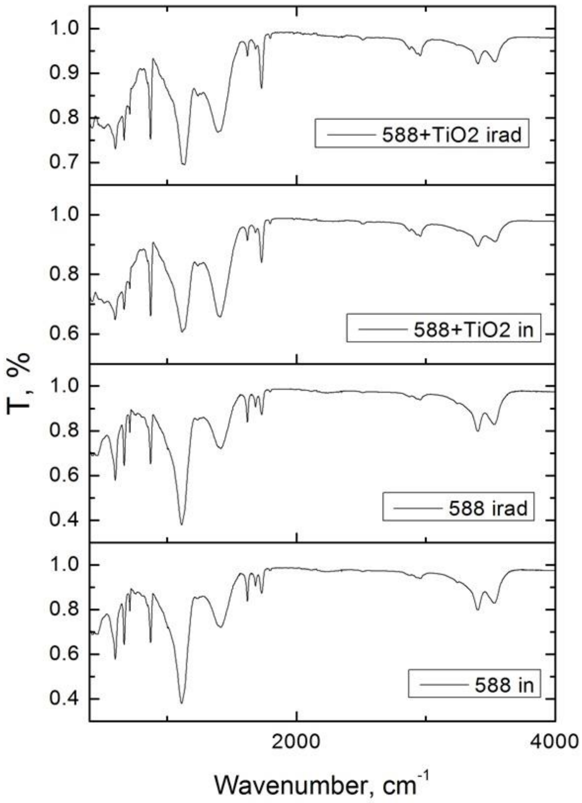
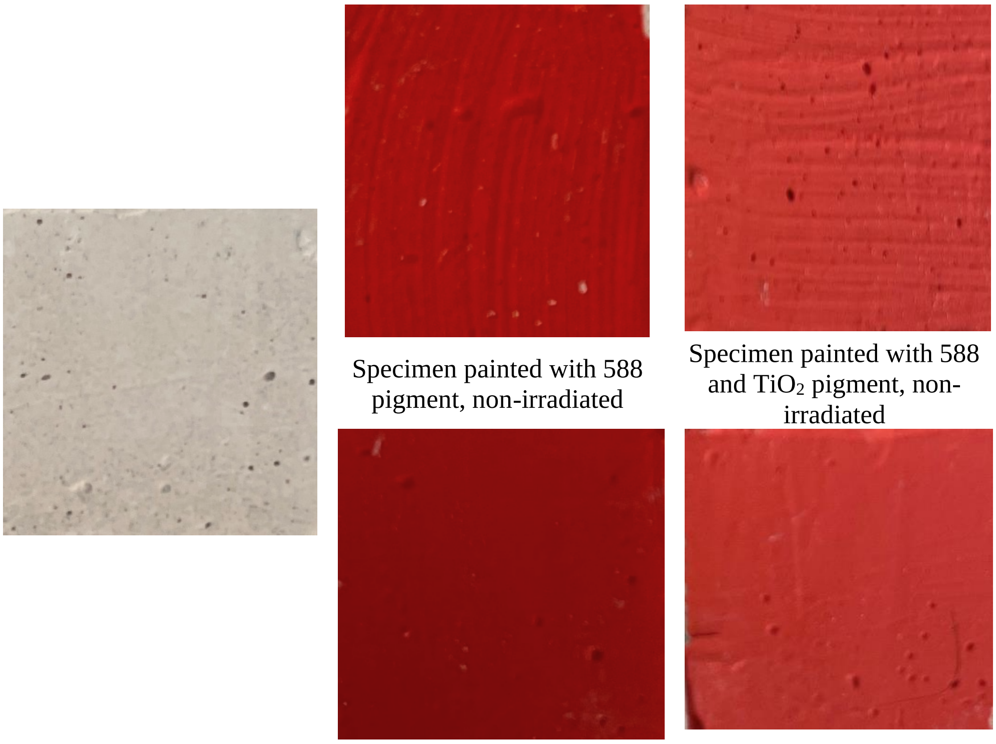


Figure 6. Raman spectra of 588 in all the experimental conditions

The **optical microscopy** investigation reveals important observations about the surface of the reference samples before aging or treatment, as well as the effects of accelerated aging and various treatments on the painted samples. Before any aging or treatments, the painted samples show a homogeneous distribution of pigment particles on the surface. There are no visible cracks or micro-cracks, and the surface is stable, indicating the pigments are well-distributed and securely bound [23, 24]. The degradation of paint films, especially those containing titanium white pigments (TiO_2), highlights the role of UV light in triggering photocatalytic processes. It effectively explains how UV exposure leads to the production of reactive radicals, causing the breakdown of the paint's oil binding medium.



Specimen painted with 588 pigment, non-irradiated

Specimen painted with 588 and TiO_2 pigment, non-irradiated

Non-treated specimen

Specimen painted with 588 pigment, irradiated 41 h with UV-lamp

Specimen painted with 588 and TiO_2 pigment, irradiated 41 h with UV-lamp

Figure 7. The optical microscopy of the painted specimens with 588 (napthol red with diaryl yellow) pigments

The degradation of paint films, particularly those containing titanium white pigments (TiO_2), is driven by photocatalytic processes initiated by UV light. When TiO_2 absorbs UV radiation, it generates highly reactive radicals that break down the oil binding medium of the paint. This breakdown leads to the formation of small volatile compounds, such as CO_2 and H_2O [25]. As the degradation progresses, a phenomenon called chalking occurs, where the pigment detaches from the binding medium [26]. In this stage, the oil binding medium begins to degrade under UV exposure. The paint's surface undergoes significant morphological changes, resulting in optical alterations, such as a noticeable decrease in gloss. Although this decrease is substantial, accurately assessing it can be difficult if the initial gloss value is not known.

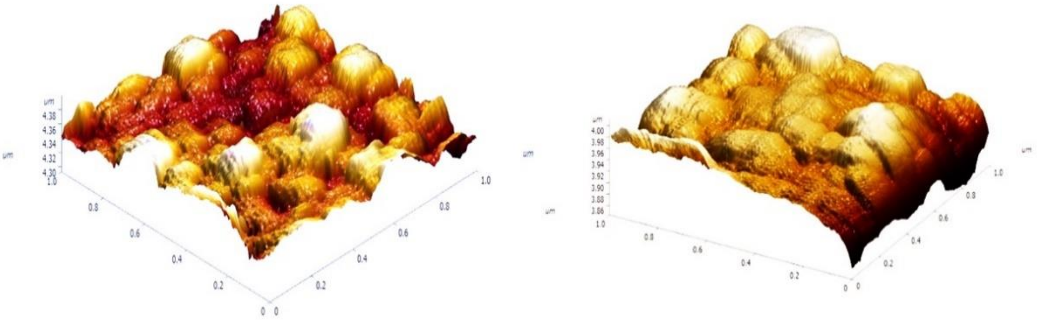


Figure 8. SEM of the painted surface: before (left) and after (right) irradiation

After irradiation, very small TiO_2 formations can be observed, unevenly distributed (Figure 8). The particles appear to be of the same size, distributed in agglomerates of various sizes. In this sense, when deposition of TiO_2 nanoparticles, no imperfections are observed in the investigated regions. The SEM images of the reference samples revealed variations in pigment grain size and heterogeneous particle distribution due to the differing grain sizes and coarseness [27]. Also, the microscopy changes could be visible by AFM, as it is shown in Figure 9.

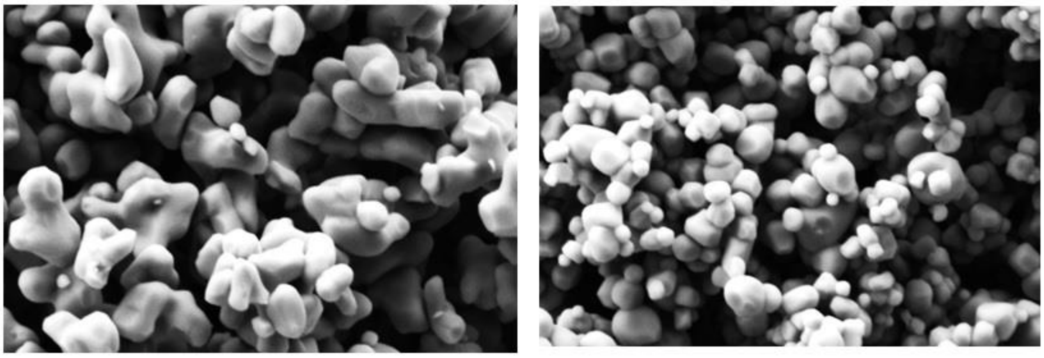


Figure 9. AFM images of 588+TiO_2 non-irradiated (left) and after irradiation (right) - 1x1 μm – mod contact

After Accelerated Aging, the surface morphology of the aged samples revealed significant alterations, including the formation of micro-cracks, bubbles and swelling and interstitial spaces between pigment grains. These changes were likely caused by the impact of accelerated artificial aging, which make the surface highly susceptible to temperature and humidity fluctuations [28]. The organization of 588+TiO_2 particles in dendrite-like formations can be observed after irradiation. A conglomerate of the particles can be highlighted, and the particle sizes between 50 – 250 nm. The AFM image shows high uniform distribution of particles with spherical shape. The AFM results show that the surface of TiO_2 is bumpy and the valleys are more than the peaks of surface [28]. The color and gloss are the most susceptible parameter in this case (Table 3).

Table 3. The CIELab parameters of the painted surface

Specimen	Parameter			
	L*	b*	b*	Gloss
588 initial	31.26	46.33	32.70	0.98
588+TiO_2	44.07	49.04	30.91	1.38
588 UV-irradiated	37.13	52.08	36.77	1.2
588+TiO_2 UV-irradiated	54.09	54.27	33.29	1.6

By irradiation, 588 supported a strongly increase of L*a*b* parameters in the absence and presence of TiO_2. This could be an explanation of a brightness (in the presence of TiO_2) and more accentuated after irradiation [29, 30].

Some changes in paint gloss resulted of chalking and provides valuable insight into how gloss can serve as an indicator of degradation. As the paint film undergoes chalking, it becomes structurally compromised and optically altered. Gloss, which serves as a key indicator of degradation, increases significantly—often nearly doubling in value—due to the chalking effect. It is an essential measure of the paint's surface condition and can be used to assess photocatalytic degradation. Gloss is closely related to surface smoothness, and the agglomeration of particles at the surface, often referred to as the "tip of the iceberg effect," leads to increased surface roughness and a decrease in gloss [31].

Conclusions

The present work addresses the effect of titanium white on some pictorial layers in mural paintings. For different type of pigment used in the painting, the effect of titanium white applied on the painting can negatively affect the quality of the pictorial layer, leading to a degradation over time of the initial color of the painting. The effects of titanium white were studied on pigment 588 and for this, some specific techniques were used such as: UV-Vis spectroscopy, Raman and infrared spectroscopy, optical microscopy, scanning electron microscopy and atomic force microscopy.

Additionally, the gloss and color of the pictorial layers were measured. The conclusion obtained is that over time, the exposure of the painting treated with titanium white to light radiation leads to a deterioration of the color and the pictorial layer, leading to its chalking. Understanding these factors and their interactions is crucial for predicting degradation rates and developing strategies to enhance the photostability of painted surfaces.

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