



# Article Bilayer Coating Composed of Starch and Methyl Cellulose-Nanoscale TiO<sub>2</sub> for the Protection of Historic Paper from UV

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**Abstract:** Among the agents of deterioration considered particularly damaging to cultural heritage objects are light, ultraviolet (UV) and infrared. The high-energy UV is the most damaging of the three, as it can cause irreversible visual, chemical and structural changes in cellulose-based materials. Known for its photocatalytic properties,  $TiO_2$  can absorb UV and is thermally and chemically stable. In this study, we propose an innovative bilayer coating composed of starch, methyl cellulose and nano- $TiO_2$  to utilize UV blocking properties of  $TiO_2$ . The results of the treatments were assessed by determining physical, optical and surface properties, as well as the degradation degree of the samples, prior and post accelerated ageing. The results show that an increase in the weight concentrations of  $TiO_2$  after accelerated ageing is closer to the original value than the colour of the uncoated ones. An increase in both the contact angle and the absorption time is also present, but after ageing, both parameters significantly decrease due to the presence of  $TiO_2$ . To conclude, the presented nanocomposite coating can protect historic paper from UV, but one should bear in mind that a higher weight concentration could lead to a higher water sensitivity after exposure to UV.

Keywords: historic paper preservation and conservation; starch; methyl cellulose; titania; accelerated ageing

# 1. Introduction

Paper-based cultural heritage objects (books, documents, art on paper, etc.) are susceptible to different forms of degradation and deterioration, which mostly occur due to biological, physical and chemical processes. The aforementioned processes are known to cause gradual and irreversible changes in the condition and appearance of historic materials.

Among the agents of deterioration [1] considered particularly damaging to cultural heritage objects are light, ultraviolet (UV) and infrared (IR). The damage caused by all three wavelength ranges occurs through oxidation. At the same time, the rate and degree of degradation depend on the quantity of photon energy absorbed during the exposure to daylight or artificial light sources.

As pure cellulose absorbs only a small portion of visible light, the most damage during daylight occurs in the spectral range between 300 nm and 550 nm [2]. Photooxidation by UV can affect the mechanical and physical properties of polymeric materials and lead to embrittlement, weakening, discolorations, reduced gloss, breaking strain, etc. [3,4]. In addition, the oxidation of cellulose promotes the formation of acids, which catalyze hydrolysis—a mechanism highly degradative to cellulose-based materials [5,6]. Therefore, to prevent the degradation of cultural heritage objects, it is crucial to control the environmental conditions under which the objects are stored, displayed or handled.

Whether to find the most effective course of action or to expand the palette of available options, new and advanced systems are continually being introduced into the field. In the



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). last few decades, nanomaterials have become omnipresent in the conservation of cultural heritage, mainly due to a good penetration into the porous structure of materials and the effectiveness in the preservation of cultural heritage objects [7,8].

During the past decade, the most commonly used nanomaterials for conserving cultural heritage objects have been alkaline earth metal oxides and hydroxides, such as titanium dioxide, zinc oxide, magnesium hydroxide, calcium hydroxide, etc. [7,9–15]. Although many other nanomaterials with diverse properties (nanocelluloses, nanoclays, nanofluids, etc.) have been extensively researched in recent years [16–18], the need to solve specific conservation problems determines both the choice of material and the methods being used.

Titanium dioxide (TiO<sub>2</sub>) is a naturally occurring oxide in three phases-anatase, brookite and rutile [19,20]. Known for its photocatalytic properties, nano-TiO<sub>2</sub> shows potential for a range of applications in the conservation of cultural heritage due to the ability to perform self-cleaning action [21,22], air-purification and odor neutralization [23], the ability to absorb/protect from UV [24] and the capacity for antimicrobial action [24,25]. However, it exhibits an inability for light absorption and photoconversion, for which various modification strategies are being developed [26,27].

Coatings in conservation may act as carriers of ingredients used for stabilizing objects [28]. As TiO<sub>2</sub> possesses thermal and chemical stability [26] and is practically white or colourless, it can be incorporated into a coating, provided there are no alterations of chemical properties and the appearance of the underlying historic materials [29].

To be considered safe for application in the cultural heritage field, a nanomaterial should display low cyto- and ecotoxicity [30]. Although there are growing concerns about the harmful effects of  $TiO_2$  [31,32], it is still considered either non-toxic [33,34] or low-toxic [35], as the long-term toxicity and environmental effects are still a subject of study [30].

Previous studies have shown that paper will degrade due to direct treatment with TiO<sub>2</sub> NPs [36,37]. However, when applied over the hydroxypropyl cellulose layer, TiO<sub>2</sub> NPs can reduce paper's photodegradation and inhibit fungal growth [37]. Although many nanomaterials (including TiO<sub>2</sub>) have been used as fillers for cellulose ethers in paper conservation studies [38–40], there is limited research carried out on the use of nanofillers for materials other than cellulose ethers [41].

Having in mind that the results of the treatment with NPs are known to be affected by both the substrate's physicochemical properties and the characteristics of materials applied (age, particle size, etc.) [42], in this research, we investigate the new coating formulations, in order to utilize the UV absorbing properties of TiO<sub>2</sub>.

Although alcohol dispersions of nanoparticles (NPs) are known for their penetration and consolidation power [42], we propose an innovative bilayer coating formulation in which the components (wheat starch, methyl cellulose and TiO<sub>2</sub>) are prepared in an aqueous solvent.

Despite the high bioreceptivity of starch [43] and the TiO<sub>2</sub>'s capacity for antimicrobial action, the prepared coatings' ability to inhibit the growth of microorganisms has not been investigated, as the study was primarily concentrated on the effectiveness of the coating formulations in protecting paper from UV.

The main goal of this research was to propose an innovative coating that will protect paper from the harmful effects of UV, and at the same time, not cause alterations in its visual appearance. The results of the treatments were assessed by determining physical, optical and surface properties, as well as the degradation degree of the samples, prior and post accelerated ageing. The findings of this research could be used as the basis for an application of the new coating formulations in the treatment of printed book pages or documents but are not appropriate for media that is not firmly bound to paper.

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## 2. Materials and Methods

For this research, Japanese handmade paper, Takogami B ( $43 \text{ gm}^{-2}$ , 70% Kozu fibre + 30% pulp, purchased from Japico-Feinpapier-Vertriebs GmbH, Vienna, Austria), and offset printing ink (NOVAVIT F918 Supreme BIO, Flint Group, Stuttgart, Germany) were used as the models of historic paper and ink. The printing ink used in this research is based on renewable raw materials (100% vegetable oil-based, alcohol-free) [44]. We have chosen the red shade, as the first printed works used red ink to demarcate sections (almanacs, religious works) or decorate title pages [45]. Japanese paper was chosen as a model substrate due to its wide use in paper conservation. However, the presence of wood pulp diminishes the quality of Japanese paper, limiting its use in paper conservation [46].

The paper samples were cut into  $250 \times 40$  mm test pieces. The red ink colour (prepared by mixing magenta and yellow process colours) was printed onto the substrate with the use of Multipurpose Printability Testing System (MZ II, Prüfbau, Peissenberg, Germany), having a printing speed of 1 m/s, printing pressure of 150 N/cm<sup>2</sup> and ink distribution time of 30 s. Printing was performed at room temperature. The proof print machine was utilized in order to achieve more uniform coverage of the surface. The obtained CIE L\*a\*b\* colour values of the dry prints were as follows: L\* = 51.16 ± 1.39; a\* = 57.25 ± 1.38; b\* = 27.36 ± 1.02.

#### 2.1. Coating Process

The printed samples were coated in a two-step process.

#### 2.1.1. The Bottom Layer

Starch was chosen for the bottom layer due to its wide use in surface sizing of paper. Furthermore, starch's viscosity can be easily adjusted with water according to the paper's grammage or texture [47].

Precooked cold-water starch was used as the test material to eliminate the time and resources needed to prepare traditional starch paste for conservation purposes. In order to make a dilute starch suspension, 7 g of precooked wheat starch (trade name wheat paste No. 301, item # TAD002001, purchased from Talas, NY, USA) was added to 100 mL of demineralized water saturated with calcium carbonate (CaCO<sub>3</sub>). The mixture was magnetically stirred for 15 min at 1000 rpm. The pH value of the prepared suspension was measured as 7.10 (determined by WTW 340 pH meter, Xylem Analytics, Weilheim, Germany).

The starch suspension was applied onto the substrate with a pipette and spread over with an automatic coating unit K Control Coater, model 202 (RK PrintCoat Instruments Ltd., Litlington, UK) at the speed of 4 m/s. The wet film deposit of 24  $\mu$ m was obtained using coating bar No. 3. The coated samples were left to air dry at room temperature.

Although the preferred methods of application in conservation include using a sprayer or a brush, we have utilized the laboratory coater to control the amount of wet film applied [48].

# 2.1.2. The Top Layer

TiO<sub>2</sub> NPs (anatase, particle size of 18 nm, purity of 99.9%) were purchased from USA (Houston, TX) Research Nanomaterials, Inc. Anatase was selected over rutile TiO<sub>2</sub> for its higher photocatalytic activity [20,49,50].

Methylcellulose (MC) solution was prepared by adding 1 g of MC powder (trade name Methyl Cellulose, item # TAD016003, purchased from Talas, NY, USA) to 100 mL of demineralized water. The prepared solution was left to settle for 24 h, before TiO<sub>2</sub> NPs were added. Four nanocomposites were prepared by adding 0.2, 0.5, 1.0 and 2.0 % w/w of TiO<sub>2</sub> NPs to MC solution, followed by ultrasonication with the Hielscher UP100H homogenizer (100% amplitude, 1 cycle) for 20, 25, 30 and 40 min, respectively. As ultrasonication raises up the temperature of the solution, during this process, the container with solution was kept immersed in a cooling water bath (Julabo GmbH, Seelbach, Germany) at 10 °C.

The top layer was applied over the dried starch layer with the K coater (coating rod No. 2, wet film deposit of  $12 \mu m$ ) at a speed of 4 m/s. The samples were air-dried.

MC used in this research is of technical grade quality [51]. Although conservation materials are expected to be as pure as possible, technical grade products are usually adequate, provided no unwanted reactions occur due to impurities present [52]. Starch and MC were combined due to their known compatibility and practical application in paper conservation treatments [53,54].

After the first analysis, samples were subjected to accelerated ageing in the test chamber Solarbox 1500 e (CO.FO.ME.GRA, Milano, Italy) with controlled temperature and UV radiation. The samples were exposed for 35 h at 50 °C, using the indoor filter.

Both the coated and uncoated samples were analyzed before and after accelerated ageing. The samples were denominated as U–uncoated samples, S–samples coated with starch only, MC–samples coated with starch and MC, iTiO<sub>2</sub>–samples coated with starch and MC-TiO<sub>2</sub> nanocomposites containing i% *w/w* of TiO<sub>2</sub>.

#### 2.2. Characterization Methods

# 2.2.1. Visual Assessment

Visual assessment was performed by observing micrographs obtained at the magnification of  $100 \times$ , using an Olympus BX51 microscope (Olympus, Tokio, Japan) with a DP72 digital camera attached.

#### 2.2.2. Colour Measurement and Fluorescence Intensity

Changes in the visual appearance of samples were assessed by measuring CIE LAB colour values, gloss levels and fluorescence intensity throughout the study. CIE L\*A\*B\* values were determined with the Techkon SpectroDens spectrophotometer (Techkon, Königstein, Germany), using the following settings: illuminant D50, a standard observer angle of 2°, M1 measuring conditions and the sample placed on a white backing. The colour differences were calculated by  $\Delta E_{ab}$  formula [55].

The fluorescence intensity was measured using the Ocean Optics USB4000+ spectrometer (Ocean Optics, Orlando, FL, USA) in conjunction with a 30 mm wide integrating sphere, under a measuring geometry of (8:di) with diffuse geometry and specular component included. The LSM Series LED light source at 365 nm was used as the fluorescence excitation wavelength, and the excitation light source was maintained at a constant current of 0.140 A. The fluorescence intensity was measured in the spectral range of 330–630 nm.

### 2.2.3. Surface Properties

As surfaces treated with  $TiO_2$  are known to drastically reduce contact angle and water absorption time [22], these parameters were determined for all samples.

The contact angle measurements were performed using the sessile drop method, for which the Dataphysics' OCA30 device and its controlling software SCA 20 were utilized. The applied redistilled water droplets' volume was set to 2  $\mu$ L, and the contact angle measurements were performed 0.2 s after the initial water-substrate contact, using the Laplace-Young fitting.

In addition, water absorption time was investigated using the camera framerate (IDS Imaging Development Systems GmbH, Obersulm, Germany) of 25 fps and utilizing a water droplet of 2  $\mu$ L, the same as for the contact angle measurement.

As both wettability and adhesion at the liquid-solid interface could be influenced by surface roughness [56,57], measurements of average roughness ( $R_a$ ) were performed using a MarSurf PS 10 device (Mahr GmbH., Goettingen, Germany). Based on the previous experience of the investigating paper with a non-uniform surface, the total length of the measurement (traversing length, Lt) was set to 15 mm, with the sampling length of 2.5 mm and the stylus speed of 1 mm/s.

# 2.2.4. Fourier Transform Infrared (FTIR) Spectroscopy

The Shimadzu FTIR IRAffinity-21 spectrometer (Kyoto, Japan) with Specac Silver Gate Evolution was used as a single-reflection ATR sampling accessory with a ZnSe flat crystal plate (index of refraction, 2.4) to measure the ATR spectra of the samples before and after UV exposure. The IR spectra were recorded in the spectral range of 4000 to 400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and were averaged over 15 scans. The spectra were vertically displayed for visual clarity.

#### 3. Results and Discussion

Figure 1 presents a microscopic image of the uncoated paper surface, magnified by  $100 \times .$  Due to the paper being handmade, there is no visible fiber direction, and the surface is not uniform. Furthermore, on the printed surface, there is a visible paper fiber network which indicates non-uniform ink film formation.







Figure 1. Micrograph of the uncoated sample (a) paper surface, (b) ink film surface.

Applying both the mono- (Figure 2a) and the bi-layer coatings (Figure 2b–d) does not affect the visual appearance of the samples' surface. Although a certain visual change caused by the application of a coating can be expected (e.g., darkening [58]), the coating materials (wheat starch and methyl cellulose) cause minimal changes as they appear transparent [59,60].

Visual assessment of the samples after accelerated ageing (further denominated as aged samples) did not show visible degradation (even at higher magnifications) and is, therefore, not presented in this work.

The colour difference of the samples is presented in Figure 3. The colour measurements were conducted after each stage presented in the methods section, including the sample preparation before and after printing (plain paper/ink film), before and after coating (uncoated/coated) and before and after accelerated ageing (unaged/aged).

The results show that the applied coatings have affected the colour of the ink, although that could not be seen on micrographs (Figure 2). It can be noticed that an increased weight concentration of  $TiO_2$  NPs in MC increases the colour difference. This behaviour could be attributed to the fact that  $TiO_2$ , although not necessarily a nano scale, is also used as a white pigment [61]. On the other hand, a slight decrease in the colour difference of the samples coated with smaller  $TiO_2$  weight concentrations could be compensation for the slight darkening of the ink film due to the coating process.



**Figure 2.** Micrograph of the ink film surface coated with (a) S, (b) S + MC; (c) S + MC + 0.2TiO<sub>2</sub>, (d) S + MC + 2.0TiO<sub>2</sub>.



Figure 3. Colour differences between the samples.

The influence of accelerated ageing was determined by observing colour changes of both the coated and the uncoated (original) samples. It is visible that an increase in the  $TiO_2$  NPs weight concentration results in a decreased colour change in aged samples. These results could be explained by  $TiO_2$ 's absorption of UV [33].

However, considering the changes caused by the coating process itself, the colour of the original ink film is the least affected by the application of  $0.2 \text{TiO}_2$ .

The fluorescence intensity measurements have confirmed that there is no response in the visible part of the spectrum, which confirms that no materials in the paper itself would exhibit a fluorescent response. Therefore, in Figure 4, only the intensities of the reflected light at a wavelength of 365 nm are shown. The uncoated paper shows the highest degree of dispersion, which is in line with expectations since the paper's surface is heterogeneous. Exposure to UV radiation leads to surface-layer degradation, resulting in greater light scattering on the fibres. Coating with S increases light absorption in the UV range. After exposing S samples to accelerated ageing, a significant increase in reflected light is visible, indicating coating degradation. The second coating (MC) reduces paper reflectance in the UV range compared to the original paper. A similar increase in reflectance is observed as in the original paper after accelerated ageing. UV absorption also depends on the size of TiO<sub>2</sub> particles. Adding TiO<sub>2</sub> affects the degree of UV reflection [62]. Previous research has found that TiO<sub>2</sub> particles strongly absorb UV radiation in the range of 330–370 nm [63], and increasing the concentration of  $TiO_2$  increases UV absorption, which accordingly decreases reflectance from the sample. Figure 4 shows no difference in reflectance between samples with 0.2% and 0.5% TiO<sub>2</sub> content. Increasing the concentration to 1% significantly reduces reflectance, and further increasing the  $TiO_2$  content reduces reflectance levels to an infinitesimal amount.



Figure 4. Fluorescence intensity of (a) ink film surface, (b) paper surface.

Interestingly, after exposure to UV radiation, the combination with 1% TiO<sub>2</sub> content proved to be the best, indicating the satisfactory filling of the space between the fibres, whose structure is not significantly compromised despite the surface layer coating breaking. By adding an ink layer, absorption is increased. By applying S, or S + MC, reflectance at 365 nm increases. With the addition of TiO<sub>2</sub>, reflectance is expected to decrease due to the absorption characteristics of TiO<sub>2</sub> NPs in the UV region. Increasing the concentration of TiO<sub>2</sub> particles from 0.5 to 1, or 2% w/w, results in a slight jump in reflection. The cause may lie in the fact that the ink, starch, MC and TiO<sub>2</sub> particles have significantly filled the space between the fibres, resulting in coating inhomogeneity and enhancing the light scattering.

The contact angle results (Figure 5) are represented as values obtained from the contact between the water droplet and the solid surface after 0.2 s, given that the water droplet is absorbed in time, as shown in Figure 6.



Figure 5. Contact angle of redistilled water on (a) ink film surface, (b) paper surface.



Figure 6. Water droplet absorption time of (a) ink film surface, (b) paper surface.

The results of the contact angle measurements show that each of the coatings has decreased the contact angle of the paper surface. On the other hand, it can be noticed that an increase in the  $TiO_2$  NPs weight concentration will slightly increase the contact angle prior to accelerated ageing, in contrast with the research mentioned above. This behaviour could be explained by the decrease in roughness (Figure 7a).



Figure 7. Roughness parameter R<sub>a</sub> on (a) ink film surface, (b) paper surface.

In addition, although the applied coatings were not visible on micrographs (Figure 2), the contact angles of the ink film and the paper surface did not differ significantly, indicating that coatings have fully covered the surface. On the other hand, the contact angles of samples coated by  $TiO_2$  nanocomposites have decreased after being subjected to accelerated ageing. In contrast, contact angles of the samples coated by S and MC have increased. The

contact angle decrease increases with the  $TiO_2$  NPs' weight concentration (Figure 5), as highlighted by the previous research [64].

In the water absorption time experiment, the addition of  $TiO_2$  NPs to a MC solution increased the water absorption time of the sample, while accelerated ageing led to its decrease (Figure 6), which is proportional to the NPs weight concentration added. On the other hand, accelerated ageing has increased the absorption time of samples coated with S and/or MC.

Compared to the results obtained from the paper surface, the water absorption times of an ink surface are shorter. This behaviour is expected, as the ink film provides an additional water barrier.

The significant decrease in water absorption time in TiO<sub>2</sub>-containing samples could be attributed to the photocatalytic activity of TiO<sub>2</sub>, where resulting radicals [65] can cause the degradation of the coating and create microcracks in the coating surface.

The results of the surface roughness measurements show higher deviations (Figure 7) due to the non-uniformity of analyzed surfaces. The other methods performed have smaller measuring resolution (the diamond tip of the perthometer measures 5  $\mu$ m in diameter, while droplets in the contact angle measurements and device's openings in optical characterization are given in mm scale).

It can be noted that accelerated ageing has increased the surface roughness of the coated samples, which could be attributed to the resulting microcracks on the coating's surface, as noted in other results as well (Figures 4–6).

In Figure 8, for the U (P), distinct vibrational bands of cellulose are depicted, such as the C–O stretching at 1105 and 1024  $\text{cm}^{-1}$  and the 1159  $\text{cm}^{-1}$  anti-symmetric bridge stretching of C–O–C groups. The most intense band at 1024 cm<sup>-1</sup> is accompanied by two peaks at 1051 and 981  $\text{cm}^{-1}$  [66,67]. These bands are present in printed paper and prints coated with S and MC (P/S and P/S/MC, respectively), although S coating (P/S) displays different vibrational bands. The bending vibration of adsorbed water is located at around  $1639 \pm 1 \text{ cm}^{-1}$  [68]. When coated with S (P/S), paper vibrational bands are present at 3420 cm<sup>-1</sup> due to the O-H hydroxyl groups, while stretching of the C-O in the C-O-H groups produces a band at 1540 cm<sup>-1</sup>. The  $\beta$ -glycosidic linkage vibration band appears at  $895 \text{ cm}^{-1}$  [66]. Additionally, the application of MC coatings alters the bands at 1370, 1340 and  $1317 \text{ cm}^{-1}$ , indicating a rearrangement of the hydrogen bonded network [66]. For the aged and unaged print, the FTIR spectrum remains relatively stable. In addition, the FTIR spectra of prints show vibrational bands of printing ink binder, which contains dispersed ink pigments. The pigments are covered with the ink binder and cannot be detected by FTIR spectroscopy. Thus, the changes occurring in the FTIR spectra due to artificial ageing result from printing ink binder degradation, not pigment degradation.



**Figure 8.** FTIR spectra of unaged and aged (AG) U, S and S + MC samples, denominated as P, P/S and P/S/MC, respectively.

When analyzing the uncoated print, vibrational bands ranging from 2925 to  $2850 \text{ cm}^{-1}$  can be attributed to aliphatic chains (CH, -CH2 and -CH3 stretching bonding vibration) present in oils such as fatty acids. Vegetable oils exhibit additional bands at  $3014 \text{ cm}^{-1}$ ,  $1463 \text{ cm}^{-1}$ ,  $1166 \text{ cm}^{-1}$ ,  $1101 \text{ cm}^{-1}$  and  $709 \text{ cm}^{-1}$ . The presence of the ester group in triglycerides is indicated by the carbonyl stretching band at  $1737-1722 \text{ cm}^{-1}$ , often accompanied by the bands at 1232 and  $1155 \text{ cm}^{-1}$ . Exposure to UV radiation causes the ester carbonyl functional group to spread in width and move towards lower wavenumbers, indicating the formation of secondary oxidation products, specifically carboxylic acids. In prints, the formation of oxidative products results in the appearance of new vibrational bands at 1649 and  $1512 \text{ cm}^{-1}$ , and the carbonyl vibrational band at  $1722 \text{ cm}^{-1}$  widens.

In the FTIR spectra of print coated with the starch-based coating (S), the presence of bound water can be indicated by the vibrational band at 1630 cm<sup>-1</sup>, while the band at 3420 cm<sup>-1</sup> can be attributed to the presence of hydroxyl groups (O–H). The stretching vibrational bands of the C–O in the C–O–H groups result in the formation of the band at 1540 cm<sup>-1</sup>. A stretching vibration of C–O is represented by the band at 1470 cm<sup>-1</sup> [69].

Applying coatings based on starch (S) and starch and MC (MC), a significant change of the FTIR spectra occurs. The change is most visible in the carbonyl spectral range at around 1730 cm<sup>-1</sup>. Due to the presence of light absorbing species and chromophore functional groups, i.e., carbonyl, resulting in the absorption of UV radiation, which are most prone to photooxidation, degradation occurs. If the carbonyl groups in polymers are covered, as seen in the FTIR spectra, a protective feature of coatings can be described [70]. Visible masking of the carbonyl groups in FTIR spectra indicates the protective feature of the proposed coatings, as detected in the colour change calculations (Figure 3).

The incorporation of  $TiO_2$  nanoparticles into the coating does not change the FTIR spectra. The masking of the carbonyl band from the printing ink binder is still present (Figure 9).



Figure 9. FTIR spectra of unaged and aged (AG) samples coated with TiO<sub>2</sub> containing coatings.

## 4. Conclusions

This research was conducted to propose new coating formulations intended to improve the protection of historic paper from UV. The coating components were prepared in an aqueous solvent, while the study design included models as representations of actual historic materials. A set of samples was coated in a two-step process (first by applying starch and afterward methylcellulose in combination with various weight concentrations of  $TiO_2$  NPs). The prepared samples were subjected to accelerated ageing in the Xenon test chamber.

By observing the results, the following conclusions were made:

The increase in the weight concentration of  $TiO_2$  NPs enhances the colour difference  $(\Delta E_{ab})$ , However, the colour of samples coated by lower concentrations of  $TiO_2$  after accelerated ageing is closer to the original value than the colour of the uncoated ones. Furthermore, the increase in the  $TiO_2$  weight concentration will also increase both the contact angle of redistilled water, and the water droplet absorption time. However, the interaction with water after accelerated ageing will significantly decrease. The decrease is proportional to the weight concentration of  $TiO_2$  added.

In conclusion, the presented nanocomposite coating can protect historic paper from UV, but a higher water sensitivity after exposure to UV should be considered. Furthermore, although the proposed coating formulations will enhance UV resistance compared to the commercial products, their applications are more complex and time-consuming.

As previous studies indicate that the presence of TiO<sub>2</sub> should improve antimicrobial properties of the coating, further research will be focused on this particular subject.

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