

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**Acrylic protective coatings modified with titanium dioxide nanoparticles: comparative study of stability under irradiation**

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/121942> since 2015-12-29T00:14:14Z

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



## UNIVERSITÀ DEGLI STUDI DI TORINO

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in *Polymer Degradation and Stability*, 97, 2136-2142, 2012, <http://dx.doi.org/10.1016/j.polymdegradstab.2012.08.014>

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), <http://www.sciencedirect.com/science/article/pii/S0141391012003394>

# **Acrylic protective coatings modified with titanium dioxide nanoparticles: comparative study of stability under irradiation**

*Dominique Scalarone\*<sup>1</sup>, Massimo Lazzari<sup>2</sup>, Oscar Chiantore<sup>1</sup>*

<sup>1</sup>Department of Chemistry and NIS Centre of Excellence, University of Torino, Via P. Giuria 7,  
10125 Torino, Italy

<sup>2</sup>Centre for Research in Biological Chemistry and Molecular Materials (CIQUS), c. Jenaro de la  
Fuente - Campus Vida, University of Santiago de Compostela, 15782 Santiago de Compostela,  
Spain

## **Abbreviated Title**

Stability of Paraloid coatings modified with TiO<sub>2</sub> nanoparticles

## **Abstract**

Acrylic coatings based on Paraloid B72 were modified with different types of titanium dioxide nanoparticles to obtain transparent, non-yellowing and chemically stable coatings, having also self-cleaning properties. To finely disperse the inorganic nanoparticles in the polymer matrix two strategies were followed: i) ex-situ functionalization of nanoparticles and ii) use of organic-inorganic coupling agents. Characterization focussed especially on the photooxidative stability of TiO<sub>2</sub> modified coatings. This is actually one of the most critical aspects of organic materials containing photoactive nanoparticles. The highly oxidant environment produced on the catalyst surface by photogenerated species is capable to mineralize many organic compounds, but in a

poorly selective way, and this often undermines the stability of the polymer that binds the photocatalyst. Improved dispersability of TiO<sub>2</sub> nanoparticles generally resulted in a diminished chemical stability of the acrylic medium, but by using tetraethoxysilane (TEOS) as a coupling agent, oxidation and cross-linking reactions were considerably reduced, ensuring better stability and reversibility in comparison to Paraloid coatings containing photoactive TiO<sub>2</sub> nanoparticles without TEOS.

## **Keywords**

Acrylic coatings; Titanium dioxide; Nanoparticles; Photodegradation; Self-cleaning

## **Introduction**

In the last decades the development of modern technologies and the intense research activity in the field of coatings have allowed the design of new products that conjugate traditional protective and decorative features with innovative properties. In addition to the many possibilities for modifying organic coatings offered by hybridization, grafting of functional groups and use of special additives, the recent developments in nanoscience have disclosed new opportunities to the production of smart coatings. Nanosized and/or nanostructured particles, if properly dispersed in coatings, can impart outstanding properties and performances, directly or after activation by external stimuli. For instance, by exposition to light photoactive materials can acquire photovoltaic properties, promote the photocatalytic degradation of volatile and water pollutants and the deactivation of micro-organisms [1-5]

Titanium dioxide (anatase), that is currently the most studied photocatalytic material, is a semiconductor with a bandgap of 3.2 eV. The absorption of photons having a higher energy than this bandgap causes the formation of a hole/electron couple. Holes of the valence band are strong

oxidants (ranging from +1.0 to +3.5V), while electrons of the conduction band are good reducing agents (ranging from +0.5 to -1.5V). Such potentials are sufficient to assure the oxidation and mineralization of many organic and inorganic contaminants [6,7]. Moreover, on the surface of the catalyst, modified by interaction with UV radiation, a hydroxylate layer forms. This layer enhances superficial wettability and provide superhydrophilic properties to the material [8,9]. In outdoor conditions, the combined effect of photodecomposition of organic/inorganic compounds and run-off gives self-cleaning properties to the surfaces. For these reasons photocatalytic materials based on TiO<sub>2</sub> have been studied extensively and some interesting products have already been introduced on the market. Most of these are opaque materials designed for applications in the field of building constructions or infrastructures, such as concrete, mortar, plaster and paints [10-13].

A major concern about organic coatings and paints containing photoactive TiO<sub>2</sub> micro- and nanoparticles is the stability over time. Oxidants adsorbed on the catalyst surface, such as hydroxyl radicals, hydroperoxyl radicals and activated oxygen species, are poorly selective and capable to mineralize many different organic compounds. This is a favorable condition as for the self-cleaning activity, but it can also undermine the stability of the polymeric matrix that binds the photocatalyst. Allen extensively investigated the photosensitized oxidation of polymers by pigmentary grade TiO<sub>2</sub> and nanosized anatase particles. His studies confirm that anatase is extremely photoactive and that anatase nanoparticles are always more active than micron-sized anatase pigments [14].

Photodegradation studies on a number of polymeric materials, including polyolefins, acrylic, alkyd, vinyl and fluorinated paints, showed a high degree of chalking of these polymers when containing nanoparticle anatase pigments [15,16]. The addition of stabilizers does not always produce beneficial effects. For instance, hindered piperidine stabilizers do not improve the stability of polymer films containing anatase and in general exhibit strong antagonism [17].

A valuable way to reduce the photocatalytic effect of TiO<sub>2</sub> is to coat particles with one or more inorganic layers such as alumina, silica or zinc oxide [14]. At present this is the preferred strategy followed in the production of many commercial TiO<sub>2</sub> pigments.

The research reported in this paper was aimed at the preparation and characterization of new formulations of acrylic coatings based on Paraloid B72 and containing anatase nanoparticles. Paraloid B72 is an extremely versatile acrylic polymer, largely used in the restoration practice as adhesive, consolidant and protective coating for a variety of substrates [18,19]. Its success as a coating material for surfaces of historical and cultural interest is due to the excellent film-forming properties, adhesion, good stability, reversibility, transparency and non-yellowing characteristics. It is therefore of great interest to explore if it is possible to combine these properties with the self-cleaning behavior. This paper compares the performances of different formulations of acrylic coatings containing TiO<sub>2</sub> nanoparticles by monitoring their photochemical stability in terms of chemical/structural modifications, weight loss, transparency, gloss and color changes. The self-cleaning capability was evaluated by observing the discoloration of graffiti under irradiation.

## **Experimental section**

**Materials.** Two commercial TiO<sub>2</sub> powders were used in this study: i) Eco Tan-A (Pentachem, Italy) is constituted by spheroidal particles of pure anatase with diameters lower than 50 nm; ii) Degussa P25 (80% anatase, 20% rutile) is mainly constituted by plate-like particles, with irregular polygonal contours and size in the 20–80 nm range (mean size ca. 30 nm).

Trimethoxy(octadecyl)silane (TMODS, 90%, Sigma Aldrich), titanium(IV) tetraisopropoxide (TTIP, 97%, Sigma Aldrich), tetraethoxysilane (TEOS, >99%, Fluka), 2-propanol (IPA, >99.8%, Sigma Aldrich), toluene (> 99.5%, Sigma Aldrich) were obtained from commercial sources.

Paraloid B72, a binary copolymer of methyl acrylate (MA) and ethyl methacrylate (EMA) in the approximate molar ratio 30:70 [20], was obtained from Rohm and Haas, Philadelphia.

**Surface functionalization of TiO<sub>2</sub> nanoparticles.** All chemicals were used without further purification. Eco Tan-A nanoparticles were dispersed in 2-propanol by ultrasonic agitation for 15

min. The derivatizing agent, i.e. TMODS, was added to TiO<sub>2</sub> in a 1:25 molar ratio, and the mixture was stirred for 16 hours at room temperature. Modified TiO<sub>2</sub> nanoparticles were recovered by centrifugation and removal of the supernatant. After three cycle of centrifugation, separation and dissolution in 2-propanol, the powder was dried overnight in a oven at 50°C.

**Preparation of Paraloid B72/TiO<sub>2</sub> nanoparticle films.** 10 mg of TiO<sub>2</sub> nanoparticles were dispersed in 1 mL of 2-propanol by ultrasonic agitation for 20 min. In order to improve the dispersion of nanoparticles proper amounts of TTIP or TEOS were eventually added. Subsequently aliquots of the dispersion were dropped in Paraloid B72 solutions prepared by dissolving 100 mg of polymer in 2 mL of toluene. Thin films were then prepared by casting the final dispersions or by spin coating, using a 8" Desk-top Precision Spin Coating System, model P-6708D vs. 2.0.

**Characterization.** Acrylic films were prepared on glass slides and let drying for at least one day at ambient conditions before analysis and ageing treatments. Once dried the acrylic films were photochemically aged in a Suntest CPS apparatus (Heraeus, Germany) equipped with a xenon lamp. In order to speed up the ageing treatment no UV filters were used and the irradiation power was set at 765 W/m<sup>2</sup>.

Transmission electron microscope (TEM) images were recorded on a Philips CM-12, working at an accelerating voltage of 100 kV. Specimens were prepared by dropping 20 µL of TiO<sub>2</sub> nanoparticles dispersion in 2-propanol solution onto carbon-coated copper grids and were imaged after complete evaporation of the solvent.

UV-Vis spectra were acquired with a Varian Cary 300 Bio UV-vis spectrophotometer.

For infrared analysis in the transmission mode, films with thickness in the range of 10-20 µm were cast on silicon wafers. Spectra were collected with a Thermo-Nicolet FT-IR Nexus instrument with a DTGS detector and a 4 cm<sup>-1</sup> resolution. Attenuated total reflectance (ATR) spectra of TiO<sub>2</sub> powders were collected with a Thermo Nicolet Smart Endurance device.

Indexes of absorption of diagnostic functional groups were used to monitor the photodegradation kinetic of acrylic films and were calculated as follows:

$$I_{\text{wn}} = \frac{(A_{\text{wn}})_t}{(A_{\text{wn}})_0} - 1$$

where A is the absorbance of the carbonyl stretching vibration measured at wavenumber wn. In this article only kinetic data of the acrylic ester group (wn=1730 cm<sup>-1</sup>) are discussed. The subscripts t and 0 refer to a generic ageing time t and to the unaged sample, respectively.

Weight losses of polymer films during degradation were determined gravimetrically. Gel content after the different treatment times was also determined gravimetrically, after soaking the sample films in toluene and collecting the insoluble fractions with vacuum filtration on 0.45 µm pre-weighted membrane filters. Data reported are the average of triplicate samples.

Color changes during photodegradation were monitored using a Minolta Chroma Meter CR-200 that was set to measure an area of 3 mm. Each measurement was repeated four times and the average value was recorded. Results were expressed using the CIELAB 1976 color system (L\*, a\*, b\*) under the standard illuminant D<sub>65</sub> and using the 10° standard observer. The device was calibrated against a white working standard supplied with the instrument. All three coordinates were measured, but only b\* (measuring the yellow-blue scale) was considered, giving the best indication of yellowing.

## Results

Table 1 describes the compositions of modified Paraloid B72 coatings containing TiO<sub>2</sub> nanoparticles. Of the two types of nanoparticles investigated in this study, Eco Tan-A is definitely more photoactive than Degussa P25. Degussa P25, that is probably the most studied nanoparticle TiO<sub>2</sub> in the scientific literature, is often used as a reference material for photocatalytic applications and also in this research was used as a reference for comparison studies.

To reduce the formation of nanoparticles aggregates two strategies were followed: (1) ex-situ functionalization of the TiO<sub>2</sub> nanoparticles with TMODS and (2) addition of organic-inorganic coupling agents (i.e., TEOS and TTIP) to the coating formulation.

The surface of TiO<sub>2</sub> nanoparticles is characterized by OH groups that, together with adsorbed water, may be appreciated by FTIR analysis through absorptions centred at approximately 3300 cm<sup>-1</sup> and 1640 cm<sup>-1</sup>. After functionalization with TMODS the Eco Tan-A powder shows other absorptions proving the presence of alkyl chains anchored on the particle surface: peaks at 2958, 2919 and 2850 cm<sup>-1</sup>, that can be assigned to stretching vibration modes of methyl and methylene groups, and a peak at 1464 cm<sup>-1</sup>, assigned to the deformation vibration of methylene. TEM images in Figure 1 show that Eco Tan-A forms very large aggregates in 2-propanol while functionalized Eco Tan-A can be better dispersed and the dimension of the aggregates is considerably reduced.

Paraloid B72/TiO<sub>2</sub> composite films were prepared as described in the experimental section. In order to establish the transparency of coatings, UV-Vis analyses were carried out. Paraloid B72 is highly transparent to visible light and does not reduce significantly transmittance with respect to glass supports. In the visible wavelength range all the UV-Vis transmission spectra of the acrylic coatings containing Eco Tan-A nanoparticles are flat, indicating the absence of specific absorptions. Only coatings containing Degussa P25 nanoparticles exhibit significant opacity up to 700 nm due to the larger mean size of the nanoparticles and to the presence of rutile, that absorbs at higher wavelengths than anatase (i.e. up to 405 nm).

Transmittance loss in the visible region was calculated with respect to the unmodified Paraloid B72 coating. Data reported in Table 2 demonstrate that most of the coatings modified with TiO<sub>2</sub> nanoparticles are substantially transparent and transmittance loss is higher than 10% only for those coatings containing Degussa P25 and 9 wt.% of Eco Tan-A. Both the addition of organic-inorganic coupling agents and functionalization of TiO<sub>2</sub> nanoparticles reduce transparency at an extent that cannot be perceived by the naked eye.

Effects of TiO<sub>2</sub> nanoparticles on the chemical stability of the acrylic coatings were studied by FTIR spectroscopy. The photooxidative behavior of Paraloid B72 was the object of a number of papers [21, 22] and the mechanisms of degradation had already been elucidated elsewhere. According to these mechanisms acrylic films of Paraloid mainly undergo oxidation and chain scission reactions. Under the severe ageing conditions applied in this work, oxidized structures appear in the polymer molecules soon after 24 h of irradiation: 1) hydroxyl groups are responsible of the broad absorptions at ca. 3500 and 3250 cm<sup>-1</sup>; 2) the carbonyl peak decreases in intensity and broadens on both sides. In particular, the inset of Figure 2 shows the changes in the carbonyl absorption indicating loss of acrylic groups (1730 cm<sup>-1</sup>), formation of carboxylic acids at ca. 1710 cm<sup>-1</sup> and of  $\gamma$ -lactones at ca. 1780 cm<sup>-1</sup>. At the same time the general and progressive decrease of the main polymer peaks reflects the volatilization of small molecules. Such decrease involves not only the ester side groups, but also the backbone structure and is in agreement with the weight loss results. Figure 3 compares the kinetic of degradation of coatings containing different types of TiO<sub>2</sub> nanoparticles by monitoring the loss of acrylic esters. The presence of Eco Tan-A nanoparticles speed up the loss of ester groups (Figure 3, left). Especially acrylic coatings containing 5 and 9 wt.% of nanoparticles degrade so fast that neither lactones nor carboxylic acids were detected and the only change in the FTIR spectra of the aged samples was a strong decrease of intensity extended to the whole spectral range. On the contrary, the curve that refers to the coating containing Degussa P25 does not differ significantly from that of the Paraloid control indicating that the kinetic of degradation of acrylic esters is not considerably influenced by Degussa P25 (Figure 3, center). Alkylation of Eco Tan-A did not improve stability and also for coatings containing only 2 wt.% of nanoparticles loss of acrylic esters was much higher and faster than for non-functionalized nanoparticles (Figure 3, right).

Figure 4 shows the effect of coupling agents on the kinetic of degradation of Paraloid B72. In general the presence of TEOS slows down the loss of ester groups. This is demonstrated by the

initial slope of the curves of Figure 4 and is especially clear for samples containing 5 and 10 wt.% of EcoTan-A (Figure 4, center).

The effect of TEOS is also confirmed by weight loss measurements (Figure 5). The acrylic film containing 3 wt.% of TEOS undergoes approximately the same weight loss of pure Paraloid and all films containing TiO<sub>2</sub> nanoparticles are stabilized by TEOS. On the contrary, TTIP reduces dramatically the polymer stability leading to almost complete degradation of coatings into volatiles within the first 250 hours of ageing. This effect is independent from the presence of TiO<sub>2</sub> nanoparticles as demonstrated by the weight loss of Paraloid B72 containing 3 wt.% TTIP that is 70% after 250 hours of ageing with respect to approximately 20% of pure Paraloid (Figure 5).

In general all coatings have similar spectra and changes occurring during the ageing treatment are qualitatively the same as described for Paraloid B72 alone, thus indicating that both TiO<sub>2</sub> nanoparticles and coupling agents essentially affect the kinetic of degradation but not the mechanisms.

The occurring of cross-linking reactions, which is not evident from FTIR spectra, was investigated by gravimetric determination of the insoluble organic fraction (Figure 6). After 300 hours of ageing the insoluble fraction of Paraloid B72 was less than 5 wt.%. TiO<sub>2</sub> nanoparticles, independently if Eco Tan-A or Degussa P25, promote cross-linking reactions resulting in the increase of the insoluble component, while acrylic coatings modified with both TiO<sub>2</sub> nanoparticles and TEOS develop a lower degree of cross-linking if compared with the corresponding formulations without TEOS.

The stability of the coatings in terms of optical properties was monitored by measurements of color and gloss changes. Gloss variation during ageing was always less than 10% and in general modified Paraloid coatings did not undergo significant color changes during ageing.

Most of the coatings can be classified as optically stable upon ageing as the slight increase in the b\* value (as well as the changes in the other coordinates) is not perceptible to the eye (Figure 7).

Also the most yellowing coatings, containing 5 and 9 wt.% of Eco Tan-A nanoparticles, underwent

a total change in the  $b^*$  coordinate ( $\Delta b^*=2$ ) confirming that they are relatively stable against yellowing. In these cases yellowing was decreased by adding TEOS to the coating formulation. In general, the effect of TEOS on color changes was negligible.

For coatings containing alkylated  $\text{TiO}_2$  nanoparticles, curves of  $\Delta b^*$  vs. ageing time are characterized by a maximum at approximately 100-150 hours of ageing followed by fast discoloration of the samples. This behavior appears to be correlated with FTIR data and especially with the kinetic of degradation of ester groups (Figure 3, right). All the coatings containing alkylated  $\text{TiO}_2$  nanoparticles underwent fast photooxidation with loss of volatiles and after 200 hours of ageing they were so degraded that acrylic ester groups were hardly detectable by FTIR. Thus, discoloration was probably due to the reduction in the coating thickness.

Preliminary indications on the self-cleaning performances were obtained by observing the discoloration of strokes of marking pens drawn on coatings and then irradiated. Red traces on coatings containing 5 wt.% of Eco Tan-A started to discolor after only 15 minutes of irradiation (Figure 8C), while Degussa P25 appeared to be less photoactive (Figure 8E) and only after 30 minutes of irradiation red strokes were clearly more discolored than those on pure Paraloid coatings. For coatings containing TEOS the self-cleaning effect was slowed down and after 15 minutes of irradiation the graffiti on coatings containing  $\text{TiO}_2$  nanoparticles and TEOS (Figure 8D,F) were substantially the same as the control sample (Figure 8B). After 60 minutes discoloration of graffiti on modified coatings, independently if containing Eco Tan-A or Degussa (Figure 8H,L), was clearly greater than the control sample (Figure 8G) and the same was for coatings containing both TEOS and  $\text{TiO}_2$  nanoparticles (Figure 8I,M). This proves that for coatings containing TEOS the self-cleaning effect is slowed down, but not completely inhibited.

## Discussion

When organic protective coatings are additivated with photoactive substances it becomes essential to assess what are the effects of the catalyst on the stability and performances of the organic component. In particular, organic coatings addressed to specific applications, e.g. the protection of works of art, must fulfill some requirements that are not always considered in products designed for other sectors, including transparency, absence of color, stability and reversibility.

Transparency and absence of color are important targets for products that must be invisible and should not alter the appearance of the surface on which they are applied. These two properties are generally not required in organic coatings, especially those for the construction industry, which in fact are often opaque.

The capability of producing transparent acrylic coatings modified with TiO<sub>2</sub> nanoparticles depends on the particle dimension and on their effective dispersion in the polymer medium. If particle size is lower than 50 nm light is transmitted and the acrylic coating retains its characteristic transparency. Eco Tan-A perfectly fulfills this first requirement but, as often occurs to nanoparticles, it is poorly dispersible and tends to form large aggregates. The low chemical affinity between organic polymers and inorganic particles makes the mechanical methods of dispersion (stirring, sonication) insufficient and a chemical approach is usually more effective. The addition of coupling agents to the film formulation and the ex-situ functionalization of the nanoparticles are two promising strategies to reduce the formation of nanoparticle aggregates and to optimize chemical interactions between inorganic nanoparticles and organic media [23,24].

Ex-situ functionalization of Eco Tan-A nanoparticles was used to control interactions with organic media. TEM images in Figure 1 and FTIR spectra of derivatised TiO<sub>2</sub> nanoparticles demonstrate that alkylation was successful and that the presence of apolar groups anchored on the nanoparticle surface prevents agglomeration and offers an efficient way to modulate surface polarity.

These nanoparticles were incorporated into the polymer matrix via solvent processing giving transparent acrylic films, sufficiently stable to color and gloss changes. On the other hand, the improved dispersability of functionalized Eco Tan-A nanoparticles ensures a larger surface area

thus maximizing the photocatalytic activity of TiO<sub>2</sub>. This results in the complete and fast degradation of the polymer matrix (Figure 3, right), making these formulations useless for coating applications.

As an alternative strategy to improve dispersability TEOS and TTIP were added to the coating formulations. The use of such organic-inorganic coupling agents was expected to protect hydroxyl functionalities on the oxide nanoparticle surface making disadvantageous those surface-surface interactions that promote the formation of agglomerates. This shielding effect, partially deactivating the photocatalyst surface, is probably the main reason for the improved stability of coatings containing TEOS, together with the possible formation of nanoscopic silica domains and of silica networks by reaction of TEOS molecules.

In fact TEOS was able to significantly improve the chemical stability of acrylic coatings containing photoactive Eco Tan-A nanoparticles. In particular, weight loss data and FTIR monitoring of the chemical structure demonstrate that scission reactions (i.e. loss of ester groups) and the formation of oxidation products (i.e., hydroxyls,  $\gamma$ -lactones, carboxylic acids) were reduced in the presence of TEOS (Figures 4 and 5). Also cross-linking reactions were considerably reduced by TEOS, thus diminishing the amount of insoluble organic component formed during ageing and improving the coating reversibility (Figure 6). This aspect is especially important for all those applications, such as conservation of cultural heritage, that require periodic removal and substitution of protective coatings. Also the stability of the optical properties (i.e., color, gloss and transmittance) of the acrylic coatings containing TEOS reflects the improved chemical stability provided by the coupling agent.

On the other hand TEOS caused a reduction of the photocatalytic activity of TiO<sub>2</sub> and this was especially evident from the degradation profiles of coatings containing Eco Tan-A, which is much more photoactive than Degussa P25. Being a mixture of anatase nanoparticles and rutile, Degussa P25 in itself is a good compromise between photoactivity, induced by anatase, and matrix stability,

due to the rutile component. Thus the addition of TEOS to formulations containing Degussa P25 appears less effective if compared to coatings modified with Eco Tan-A (Figure 4, right). Why the effect of TTIP is so different from TEOS, resulting in the complete degradation of the acrylic coatings in approximately 250 hours of ageing, is still something that has to be clarified. Reasonably it is not related only to a better deagglomeration of TiO<sub>2</sub> nanoparticles, but it may also be speculated that TTIP, by a direct effect or through the in situ formation of nanosized TiO<sub>2</sub> aggregates [25], acts as a photosensitiser.. The weight loss registered during the ageing of Paraloid coatings containing TTIP and without TiO<sub>2</sub> nanoparticles confirms this hypothesis (Figure 5). Reducing the photocatalytic activity of TiO<sub>2</sub>, TEOS also retards the photodegradation of organic dirt deposited on the surface of acrylic coatings modified with TiO<sub>2</sub> nanoparticles. However, after 60 minutes of ageing graffiti drawn on acrylic coatings containing 5 wt.% of Eco Tan-A were greatly discolored, while the degradation profile of the acrylic medium is comparable to that of pure Paraloid coatings. This is an important result because demonstrates that under the severe ageing conditions applied in this study, and despite the poor selectivity of photoactive TiO<sub>2</sub> nanoparticles, Paraloid coatings modified with TiO<sub>2</sub> nanoparticles and TEOS show self-cleaning properties and at the same time maintain transparency, non-yellowing characteristics, chemical stability and also good reversibility.

## **Conclusions**

Coatings based on Paraloid B72, an acrylic polymer well known in the restoration practice, were modified with photoactive titanium dioxide nanoparticles. Different formulations, including different types of TiO<sub>2</sub> nanoparticles (DegussaP25 and Eco Tan-A), alkylated nanoparticles and coupling agents (TEOS and TTIP), were developed and tested in order to assess the effects of the catalyst on the photooxidative stability of the acrylic component and possible applications as self-cleaning materials.

The characterization of the new coatings focused on aesthetic features, such as transparency, gloss and color changes, and on the stability of the chemical structure.

Combining the results of the chemical and optical characterization with the discoloration of graffiti drawn on the coating surface, it is clear that anatase nanoparticles are effective in catalysing photodegradation reactions, but in a poorly selective way. In this context, coating formulations including both TiO<sub>2</sub> nanoparticles and TEOS appear to be a good compromise between self-cleaning power and stability of Paraloid B72 coatings.

Of course many concerns still exist on the real applicability of these products in the restoration practice. However, the possibility to improve the stability of acrylic coatings containing photoactive nanoparticles and to extend the results obtained in this research to other polymer materials appears to be of great interest not only for conservation treatments but for the coating industry in general.

## References

1. O'Regan B, Grätzel M. A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. *Nature* 1991, 353:737–740.
2. Bowering N, Walzer GS, Harrison PG. Photocatalytic decomposition and reduction reactions of nitric oxide over Degussa P25. *Appl Catal B* 2006; 62:208-216.
3. Augugliaro V, Palmisano L, Schiavello M, Sclafani A, Marchese L, Martra G, Miano F. Photocatalytic degradation of nitrophenols in aqueous titanium-dioxide dispersion, *Appl Catal* 1991; 69:323-340.
4. Fu G, Vary PS, Lin CT. Anatase TiO<sub>2</sub> nanocomposites for antimicrobial coatings. *J Phys Chem B* 2005; 109:8889–8898.
5. Han SJ, Choi SH, Kim SS, Cho M, Jang B, Kim DY, Yoon J, Hyeon T. Low-temperature synthesis of highly crystalline TiO<sub>2</sub> nanocrystals and their application to photocatalysis. *Small* 2005; 1:812–816.

6. Hoffmann MR, Martin TS, Choi W, Bahenemann DW. Environmental Applications of Semiconductor Photocatalysis. *Chem Rev* 1995; 95:69-96.
7. Fujishima A, Zhang X, Tryk DA. TiO<sub>2</sub> photocatalysis and related surface phenomena. *Surf Sci Rep* 2008; 63:515-582.
8. Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, Kitamura A, Shimohigoshi M, Watanabe T, Light-induced amphiphilic surfaces. *Nature* 1997; 388:431-432.
9. Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, Kitamura A, Shimohigoshi M, Watanabe T, Photogeneration of highly amphiphilic TiO<sub>2</sub> surfaces. *Adv Mater* 1998; 10:135-138.
10. Zhao X, Zhao Q, Yu J, Liu B. Development of multifunctional photoactive self-cleaning glasses. *J Non-Cryst Solids* 2008; 354:1424-1430.
11. Rairez AM, Demeestere K, De Belie N, Mantyla T, Levanen E. Titanium dioxide coated and cementitious materials for air purifying purposes: preparation, characterization and toluene removal potential. *Build Environ* 2010; 45:832-838.
12. <http://www.italcementigroup.com/ENG/Research+and+Innovation/Innovative+Products>, 2012.
13. <http://www.mmc.co.jp/corporate/en/product/construct/10.html>, 2012.
14. Allen NS, Edgea M, Ortega A, Sandovala G, Liauwa CM, Verrana J, Strattonb J, McIntyre RB. Degradation and stabilisation of polymers and coatings: nano versus pigmentary titania particles. *Polym Degrad Stab* 2004; 85:927-946.
15. Allen NS, Edge M, Corrales T, Catalina F. Stabiliser interaction in the thermal and photooxidation of titanium dioxide pigmented polypropylene films. *Polym Degrad Stab* 1998; 61:139-149.
16. Allen NS, Edge M, Verran J, Stratton J, Maltby J, Bygott C. Photocatalytic titania based surfaces: Environmental benefits. *Polym Degrad Stab* 2008; 93:1632-1646.
17. Allen NS, Edgea M, Ortega A, Liauwa CM, Strattonb J, McIntyre RB. Behaviour of nanoparticle (ultrafine) titanium dioxide pigments and stabilisers on the photooxidative stability of water based acrylic and isocyanate based acrylic coatings. *Polym Degrad Stab* 2002, 78:467-478.

18. Horie CV. *Materials for Conservation: Organic Consolidants, Adhesives and Coatings*. Oxford: Butterworth-Heinemann, 1987.
19. Feller RL, Curran M, Bailie C. In: Pappas SF, Winslow FH, editors. *Photodegradation and photostabilization of coatings*, ACS symposium series 151, Washington, DC: American Chemical Society, 1981. p. 183-196.
20. Chiantore O, Lazzari M. Characterization of acrylic resins. *Int J Polym Anal Charact* 1996; 2: 395-408.
21. Chiantore O, Lazzari M. Photo-oxidative stability of paraloid acrylic protective polymers. *Polymer* 2001; 42:17–27.
22. Chiantore O, Trossarelli L, Lazzari M. Photooxidative degradation of acrylic and methacrylic polymers. *Polymer* 2000; 41:1657–1668.
23. Schmidt H, Naumann M, Muller TS, Akarsu M. Application of spray techniques for new photocatalytic gradient coatings. *Thin Solid Films* 2006; 502:132-137.
24. Koziej D, Fischer F, Kranzlin N, Caseri WR, Niedeberger M. Nonaqueous TiO<sub>2</sub> nanoparticle synthesis: a versatile basis for the fabrication of self-supporting, transparent, and UV-absorbing composite films. *ACS Appl Mater Interfaces* 2009; 1(5): 1097-1104.
25. Scalarone D, Tata J, Caldera F, Lazzari M, Chiantore O. Porous and worm-like titanium dioxide nanostructures from PS-b-PEO block copolymer micellar solutions. *Mater Chem Phys* 2011; 128:166–171.

## Figure Captions

Figure 1. TEM images of Eco Tan-A TiO<sub>2</sub> nanoparticles dispersed in 2-propanol before (left) and after functionalization (right). Scale bars correspond to 500 nm.

Figure 2. FTIR spectral changes of Paraloid B72. Arrows indicate absorptions that increase in intensity during ageing (↑) or decrease (↓).

Figure 3. FTIR absorption of acrylic esters at 1730 cm<sup>-1</sup> vs. ageing time. Acrylic coatings containing: Eco Tan-A nanoparticles (left); Degussa P25 nanoparticles (center); alkylated Eco Tan-A nanoparticles (right).

Figure 4. FTIR absorption of acrylic esters at 1730 cm<sup>-1</sup> vs. ageing time. Effect of TEOS on the chemical stability of: Paraloid B72 acrylic coatings (left); acrylic coatings modified with Eco Tan-A nanoparticles (center); acrylic coatings modified with Degussa P25 nanoparticles (right).

Figure 5. Weight loss vs. ageing time. Effect of coupling agents (TEOS, TTIP) on the stability of Paraloid B72 acrylic coatings.

Figure 6. Insoluble organic fraction of acrylic coatings after 300 hours of ageing.

Figure 7. Color change vs. ageing time for Paraloid B72 coatings containing TiO<sub>2</sub> nanoparticles and TEOS.

Figure 8. Discoloration of graffiti drawn on Paraloid coatings modified with TiO<sub>2</sub> nanoparticles. Framed images correspond to the coatings showing the best compromise between self-cleaning performances and stability.

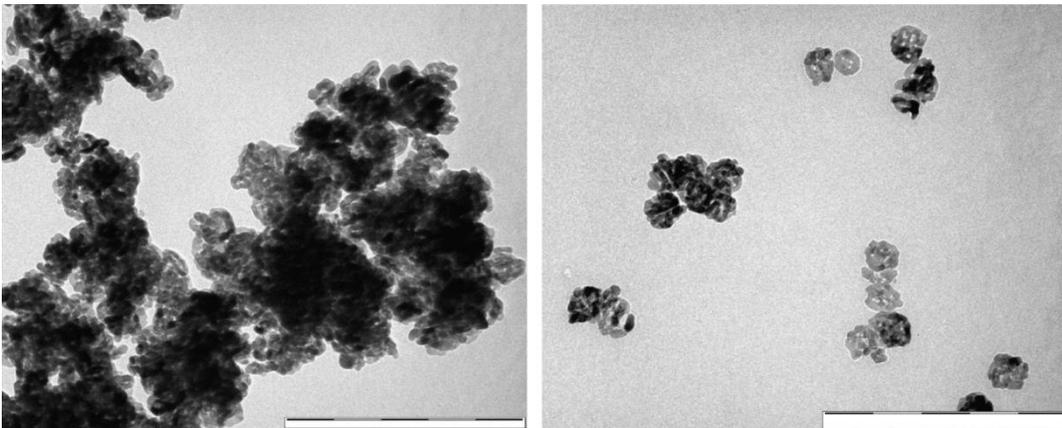
**Table 1. Compositions (wt.%) of Paraloid B72 films modified with coupling agents and TiO<sub>2</sub> nanoparticles**

Sample name	Paraloid B72	TiO <sub>2</sub> nanoparticles			Coupling agent	
		Eco Tan-A	Alkylated Eco Tan-A	Degussa P25	TEOS	TTIP
B72 + EcT2	98	2				
B72 + EcT5	95	5				
B72 + EcT9	91	9				
B72 + EcTAlk2	98		2			
B72 + EcTAlk5	95		5			
B72 + EcTAlk9	91		9			
B72 + Deg5	95			5		
B72 + TEOS	97				3	
B72 + EcT2 + TEOS	95	2			3	
B72 + EcT5 + TEOS	92	5			3	
B72 + EcT9 + TEOS	88	9			3	
B72 + Deg5 + TEOS	92			5	3	
B72 + TTIP	97					3
B72 + EcT2 + TTIP	95	2				3
B72 + EcT5 + TTIP	92	5				3

**Table 2. Transmittance loss in the visible range (400-800 nm) calculated with respect to Paraloid B72 .**

Sample name	Transmittance loss (%)
Paraloid B72 + EcT2	0,2
Paraloid B72 + EcT5	2,4
Paraloid B72 + EcT9	5,9
Paraloid B72 + EcTAlk2	3,6
Paraloid B72 + EcTAlk5	4,0
Paraloid B72 + EcTAlk9	7,0
Paraloid B72 + Deg5	10,0
Paraloid B72 + TEOS	3,6
Paraloid B72 + EcT2 + TEOS	4,0
Paraloid B72 + EcT5 + TEOS	5,7
Paraloid B72 + EcT9 + TEOS	18,2
Paraloid B72 + Deg5 + TEOS	12,5
Paraloid B72 + TTIP	0,2
Paraloid B72 + EcT2 + TTIP	3,9
Paraloid B72 + EcT5 + TTIP	9,9

**Figure 1**



**Figure 2**

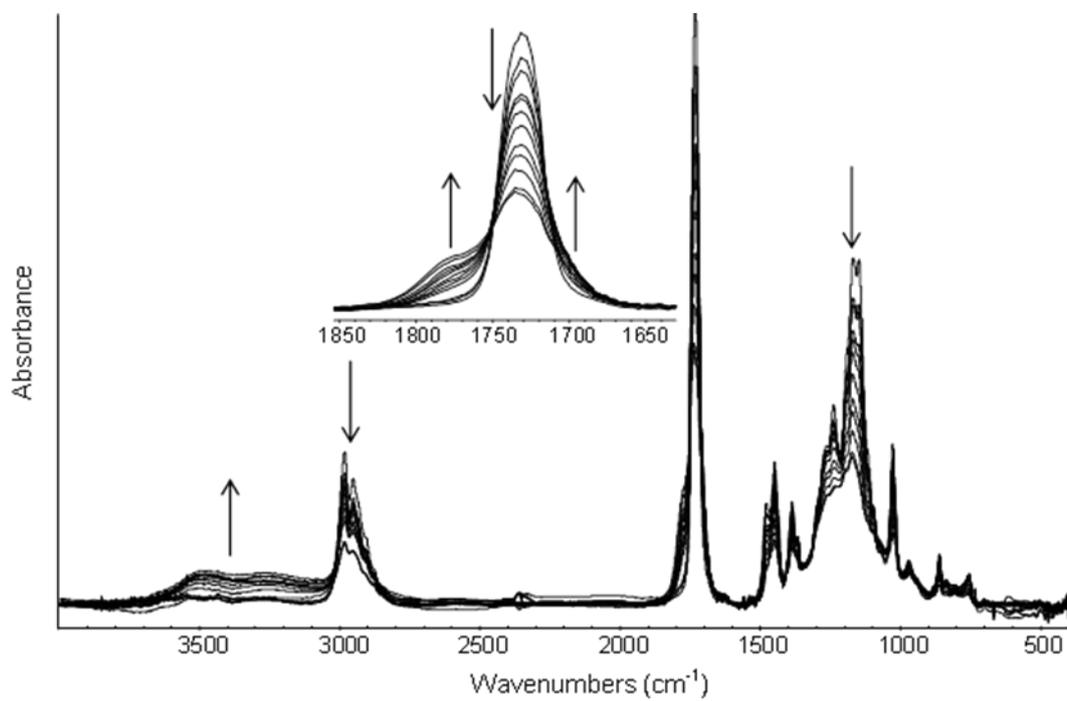


Figure 3

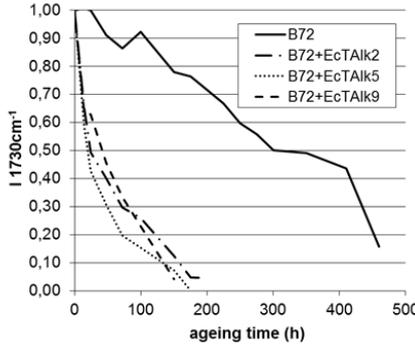
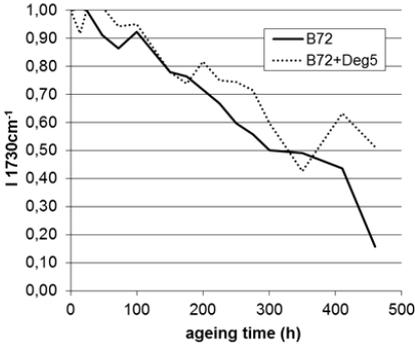
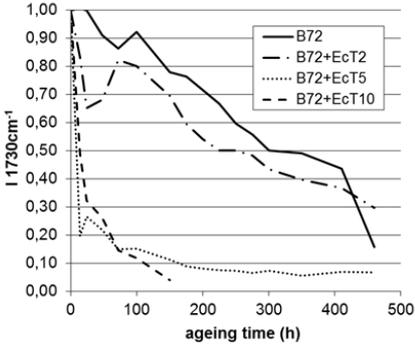
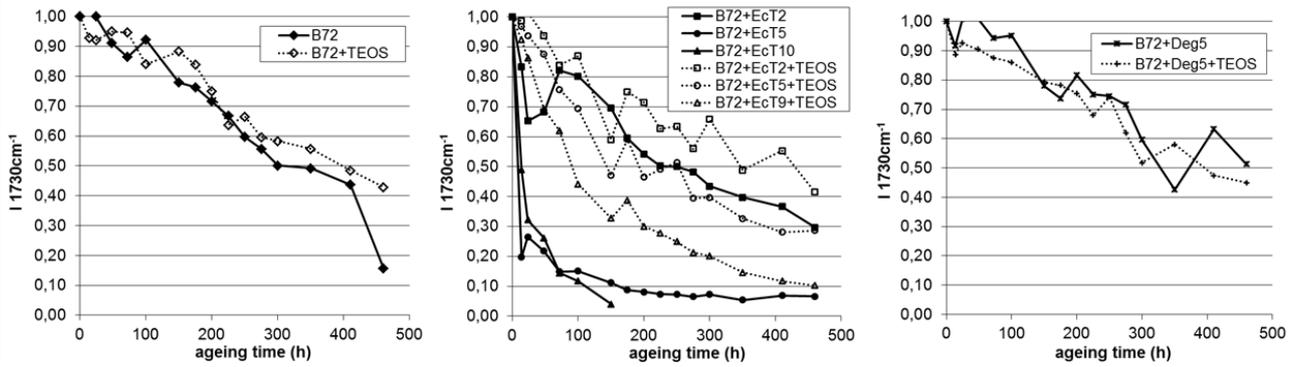
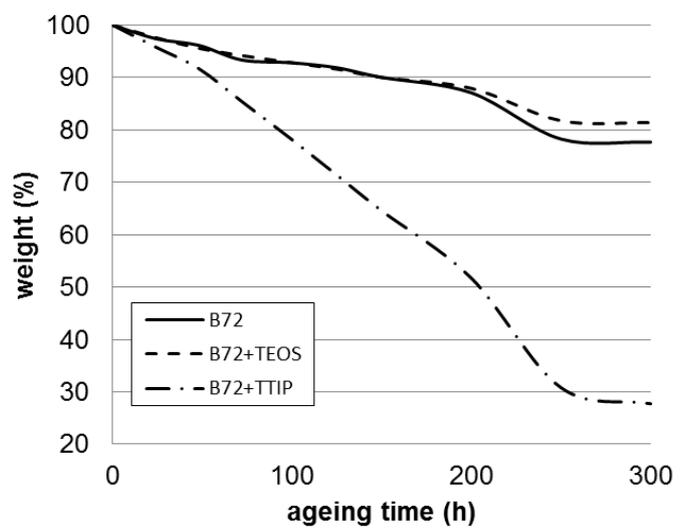


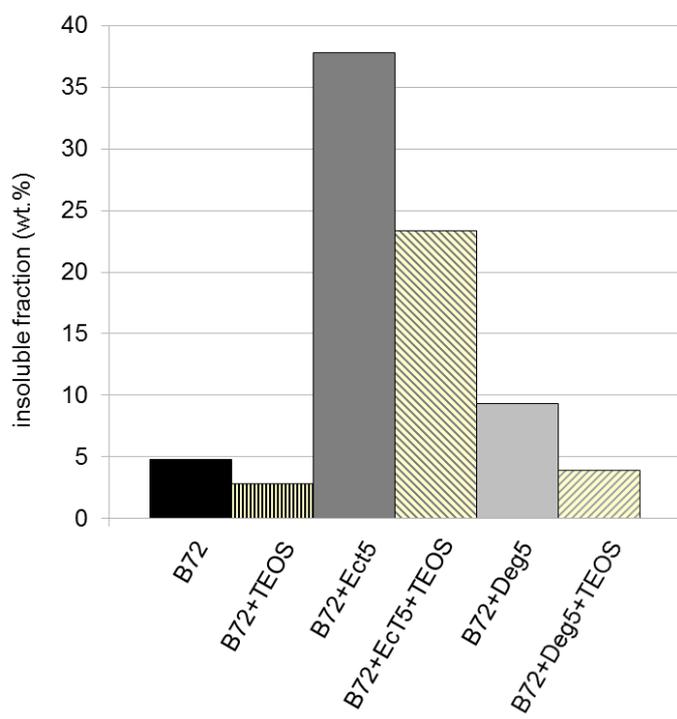
Figure 4



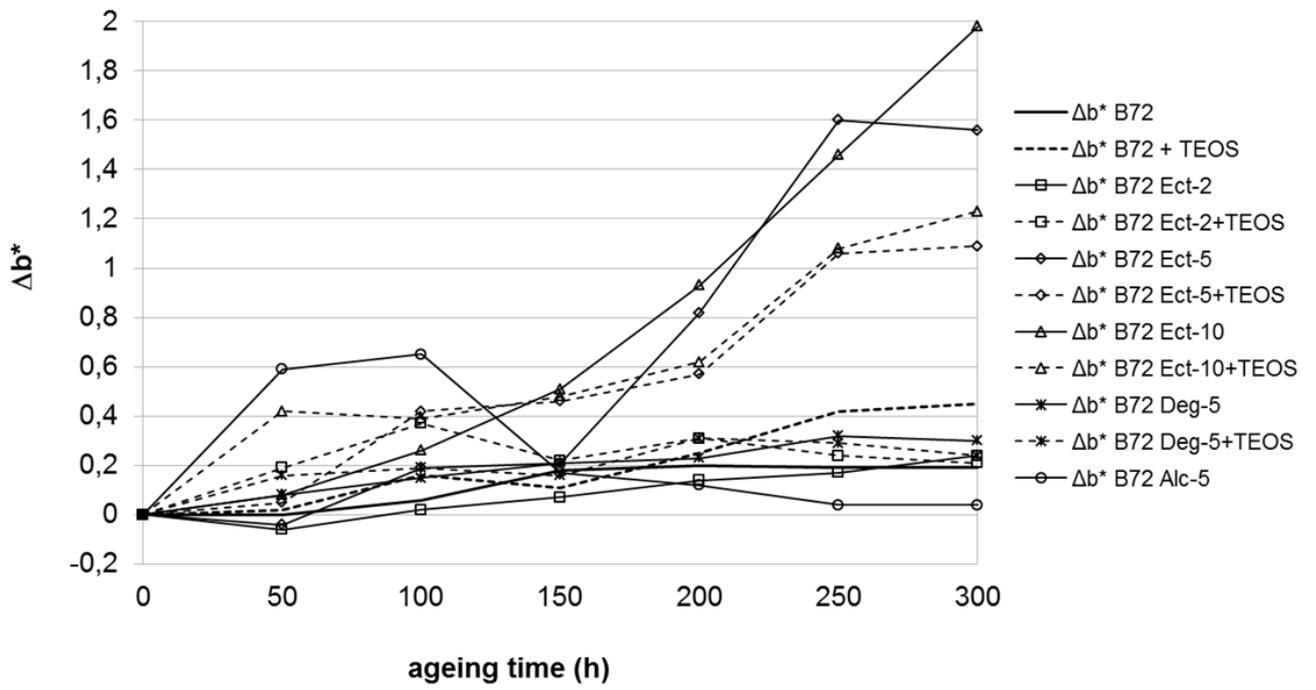
**Figure 5**



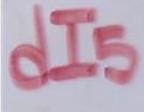
**Figure 6**



**Figure 7**



**Figure 8**

Non irradiated	Irradiated 15 min				
A) Paraloid B72	B) Paraloid B72	C) B72+EcT5	D) B72+EcT5+TEOS	E) B72+Deg5	F) B72+Deg5+TEOS
					
	Irradiated 60 min				
	G) Paraloid B72	H) B72+EcT5	I) B72+EcT5+TEOS	L) B72+Deg5	M) B72+Deg5+TEOS
					