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FULL PAPER

THE PROTECTIVE ROLE OF TITANIUM DIOXIDE PIGMENTS ON PICTORIAL ARTWORKS IN CONTAMINATED INDOOR ENVIRONMENTS

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Recently, heterogeneous photocatalytic detoxification methodologies proved very promising for the treatment and disinfection of contaminated air. It is well established that initiation of photocatalytic degradation of paint layers containing TiO_2 is quite different from that of layers without TiO_2. Since TiO_2 is broadly used in modern and contemporary pictorial art, acting both as a pure white pigment or a moderator of hue and saturation, the present paper is trying to investigate the dioxide's role in the inherent protection of polychrome works of art, proposing an additional application of heterogeneous photo catalytic decomposition (TiO_2/UV-A). For testing the possibility, Hansa yellow and verdigris were selected as two colourants bearing extensively studied degradation processes, and having structures easily correlated to further chemically related pigments. Various types of TiO_2, in rutile form or as a mixture of rutile/anatase, were examined at several light intensities as to their role in protecting or not Hansa yellow and verdigris. In order to reproduce a sequence of typical indoor environments, the induced difference was measured with reference to samples not containing TiO_2 on a series of experimental simulations of paintings at various proportions of TiO_2/colourant, placed in an isolated chamber filled with contaminated air and irradiated.

1 Introduction

Pictorial works of art, exhibited or stored, are susceptible to environmental factors, and alterations occur with the passage of time. To achieve a better and more effective preservation, the behaviour of all materials involved should be clarified. In this frame, the impact of humidity, temperature, ultraviolet radiation, or pollutants on the painting's chromatic profile proved of primary importance, as a most apparent result of non-controlled external conditions.

The present article is concerned about the future performance of pigments used in modern and contemporary painting in combination with

titanium dioxide, and applied with poly(vinyl acetate), a binding medium commonly used by artists during the second half of the 20th century. It is based on studies dealing with the effect of light and atmospheric pollutants on the fading of natural and synthetic colourants,[1-3] on the colour and molecular structure of inorganic colourants,[4-7] on the molecular structure of organic and inorganic colourants in an oil binding medium,[8,9] and on the colour of paint layers using protein,[10] acrylic copolymers, [11-16] and poly(vinyl acetate)[17,18] as binding media. A further significant point of reference are studies dealing with the effect of light on the structure of coatings pigmented with titanium dioxide.[19-22] A systematic comparative review of all colourimetric and spectroscopic data permits evaluating the pigments as to compatibility and stability towards extrinsic factors, and is proposing degradation routes at a molecular level, with the intention of contributing to the physicochemical elucidation and appropriate preservation of contemporary polychrome works of art based on poly(vinyl acetate) paints.

2 Materials and Methods

2.1 Preparation of Experimental Tables

Hansa yellow PY74 and verdigris (Kremer Pigmente) are applied with poly(vinyl acetate) (Arvanco) as homogenous layers – thickness 150µm – on inert glass ground devoid of preparation. The two synthetic pigments have been selected because they are largely known as commercial products, while bearing extensively studied degradation processes, and having structures easily correlated to further chemically related colouring compounds.

sample	colourant	rutile [g]	rutile/ anatase [g]	proportion (g pigment / g TiO_2)	poly (vinyl acetate) [ml]	water [ml]
	PY74 [g]					
1	2.625	2.625		1:1	5.40	3.80
2	1.33	3.99		1:3		
3	3.99	1.33		3:1		
3	2.625		2.625	1:1		
5	1.33		3.99	1:3		
6	3.99		1.33	3:1		
	verdigris [g]					
7	2.625	2.625		1:1	5.40	3.80
8	1.33	3.99		1:3		
9	3.99	1.33		3:1		
10	2.625		2.625	1:1		
11	1.33		3.99	1:3		
12	3.99		1.33	3:1		

Table 1: Composition of Experimental Tables.

Since TiO_2 is broadly used in modern and contemporary pictorial art, acting both as a pure white pigment or a moderator of hue and saturation, the present paper is trying to investigate the dioxide's role in the inherent protection of polychrome works of art. The synthetic pigments applied either alone or mixed with titanium dioxide, in the form of rutile or as a mixture of the forms rutile/anatase (P-25 Degussa, anatase/rutile mass ratio 3.6/1, surface area 56 m^2g^{-1}, nonporous) in various proportions pigment/TiO_2, as listed in Table 1.

2.2 Artificial Ageing

After a one-month drying period, the experimental tables were subjected to the ageing tests in a Voetsch VC0018 climatic chamber for a total time of thirty days. The experimental tables were exposed inside the chamber to Philips Cleo 20 W fluorescence tubes, which emit highly concentrated ultraviolet radiation in the 300-400 nm range, peaking at ~350 nm, a wavelength transparent to window panel glass and thus preferable for testing materials related to conservation.[23] The samples were placed at a distance of 25 cm from the radiation source, and the average intensity measured was 1.7 mW/cm^2. The temperature was kept constant at 30°C and the relative humidity at 50%. In addition, during the process the samples were exposed to sulphur dioxide vapours at an overall concentration of approximately 20 ppm.

The resulting tables were subjected to colourimetric and spectroscopic measurements at regular intervals.

2.3 Colourimetry

A Miniscan XE Plus spectrophotometer (HunterLab) was used for the colour measurements during the accelerated ageing. The colour changes of paint layers were expressed using the colour space CIE 1976 (L*a*b*). The total colour difference ΔE*, for 10° standard observer and standard illuminant D_{65}, between the sample prior to ageing exposure and at each measurement during the ageing was calculated according to the equation: $\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}$.

2.4 Reflectance Micro-FTIR Spectroscopy

In order to determine the degree, in which chemical and molecular alterations are related to colour

changes, infrared spectra of paint layers before and after ultraviolet exposure were recorded.

FT infrared spectra were recorded on a Perkin Elmer Spectrum GX II spectrometer equipped with a MCT detector. The spectra were collected in specular reflectance mode in the range of 4000-700 cm^{-1}, with a resolution of 4 cm^{-1}, an aperture of 100x100 μm, and 150 scans per measurement. Five spectra from different areas of each sample were recorded; the average spectrum was calculated and transformed in transmission mode by the Kramers – Kronig algorithm.

3 Results and Discussion

Hansa yellow PY74 – pure or mixed with titanium dioxide – experimental tables were subjected to the influence of ultraviolet radiation and sulphur dioxide vapours at ambient conditions. In painting layers containing rutile the maximum in reflectance spectra / visible region is hardly shifted. The reflectance values of paint layers containing rutile slightly decrease between 500 and 625 nm, and then slightly increase when moving further to higher wavelengths (Figure 1 a, c, e, g, h). In the same frame, Δb* slightly increases, while ΔL* was as well barely decreasing (Figure 2). In painting layers containing rutile/anatase alterations are much more significant, and the maximum in reflectance spectra / visible region is shifted from 500 nm to 625 nm already during the first three days. Reflectance values decrease in the larger part of the visible spectrum, with more intense decline in the yellow region, 550-600 nm (Figure1 b, d, f, h). In the same frame, Δb* values greatly decrease, similarly as does ΔL*. As the quantity of rutile/anatase augments in the paint layer, the colour change increases. Thus, the layer

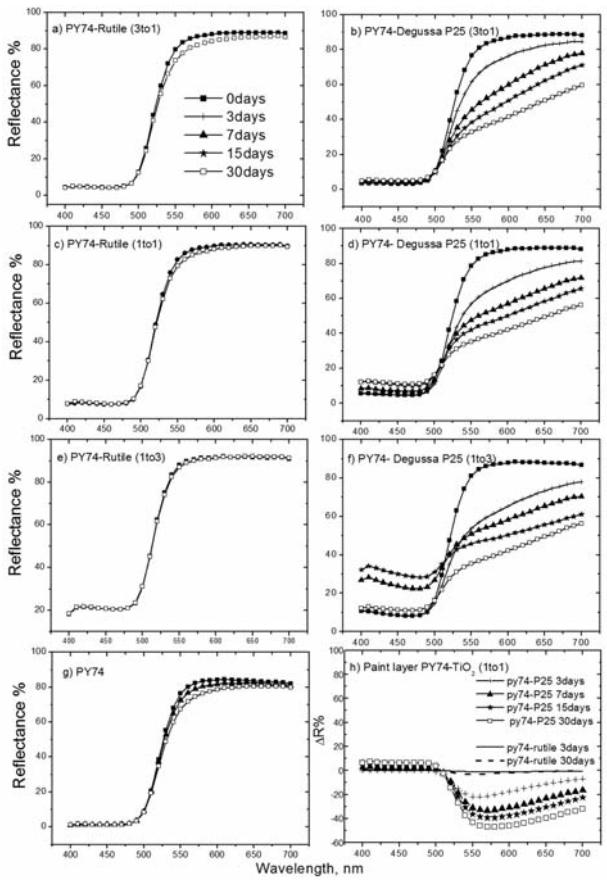

Figure 1: Reflectance spectra in visible region of untreated and artificially aged paint layers of a) Hansa yellow PY74 mixed with rutile in proportion 3 to 1; b) Hansa yellow PY74 mixed with rutile/anatase in proportion 3 to 1; c) Hansa Yellow PY74 mixed with rutile in proportion 1 to 1; d) Hansa Yellow PY74 mixed with rutile/anatase in proportion 1 to 1; e) Hansa Yellow PY74 mixed with rutile in proportion 1 to 3; f) Hansa yellow PY74 mixed with rutile/anatase in proportion 1 to 3; g) pure Hansa yellow PY74; h) Reflectance spectra in visible region of artificially aged paint layers of PY74 mixed with TiO2 in proportion 1 to 1, reported as difference spectra ($\Delta R=R_{aged} - R_{untreated}$).

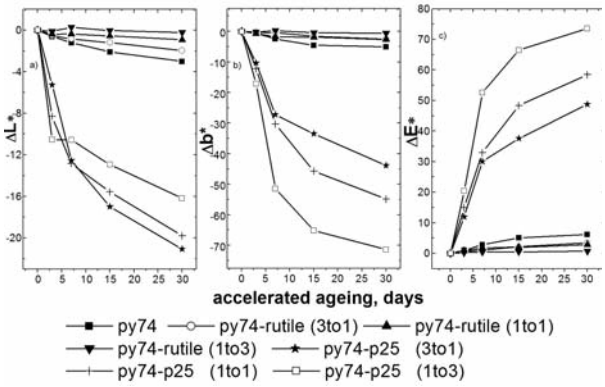

Figure 2: a) ΔL*, b) Δb* and c) ΔE* changes of paint layers of pure PY74 and of PY74 mixed with TiO2, during artificial ageing.

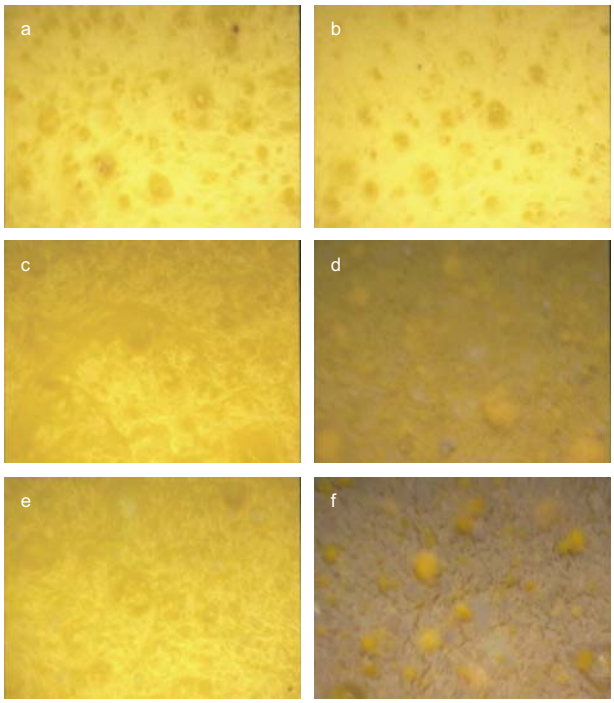

Figure 3: Surface photographs of Hansa yellow P74 paint layers; a: rutile 1:1, untreated; b: rutile 1:1, 15 days; c: rutile/anatase 1:1, untreated; d: rutile/anatase 1:1, 15 days; e: rutile/anatase 1:3, untreated; f: rutile/anatase 1:3, 15 days.

containing PY74 – rutile/anatase in proportion 3 to 1 reached a colour difference ΔE*=50, for 1 to 1 the colour difference was ΔE*=60 and for 1 to 3 ΔE*=70 (Figure 2).

The pigment proved rather stable towards accelerated ageing when rutile was present, the colour change to a brown hue actually occurring solely in presence of rutile/anatase (Figure 3). No qualitative changes, which would correspond to molecular structure modification as a result of accelerated ageing, are observed in the FT infrared spectra of untreated and aged paint layers of PY74 and PY74 mixed with rutile. Solely a small intensity decrease in the ester group peaks (1739, 1374 and 1243 cm^{-1}) of the poly(vinyl)acetate medium is noticed, due to their decomposition. The intensity of the pigment peaks remained stable even after 30 days of ageing (Figure 4).

Therefore, the pigment Hansa yellow PY74 proved rather stable. Generally, colour properties depend largely on the crystallographic arrangement of the molecule. Thus, the side groups in *o*-position on both phenyl groups causing intra molecular hydrogen bonds tend to hold the molecules approximately planar, permitting them to stack within the crystal in packed columns linked by van der Waals forces. These intra molecular bonds are responsible for the photo stability of PY74.[24]

Alternatively, the presence of photoactive rutile/anatase results in gradual degradation of the medium (PVAc). Indeed, after fifteen days of ageing the C=O stretching peak at 1740 cm^{-1} disappears, while the peaks at 1375 cm^{-1} and 1248 cm^{-1}, corresponding to the C–H bending and C–O stretching bands, are hardly discernable (Figure 5). After 15 days of ageing, FT infrared spectra of PY74 – rutile/anatase (in proportion 3 to 1) are characterized only by PY74 peaks, PVAc peaks having disappeared. Furthermore, and in accordance with the aforesaid arguments, the intensity of PY74 peaks remains stable even after 30 days of ageing as a result of its photo-stability (Figure 5 a). The degradation rate is directly proportional to the ratio of titanium dioxide in the paint layer. When a large quantity of rutile/anatase is present, the spectra of pigment and binding medium are not discernable, as the peaks corresponding to the C–H stretching bands turn to a broad shoulder (Figure 5). The results permit the assumption that the rutile form of titanium dioxide protects the paint layer from degradation, while the rutile/anatase form (P25 Degussa) is further accel-

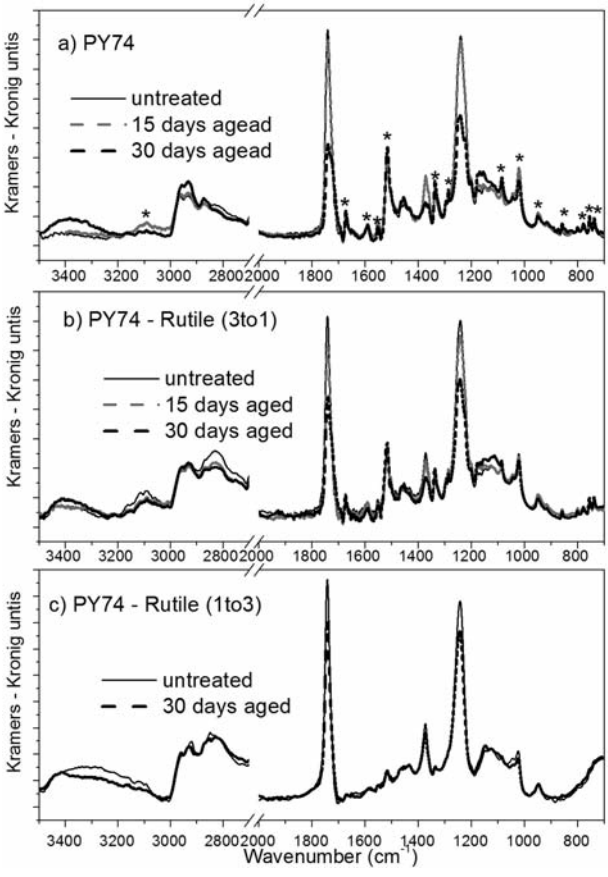

Figure 4: FT-IR reflectance spectra of paint layers of a) Hansa yellow PY74; b) PY74 mixed with rutile in proportion 3 to 1: and c) PY74 mixed with rutile in proportion 1 to 3, before and after ageing.

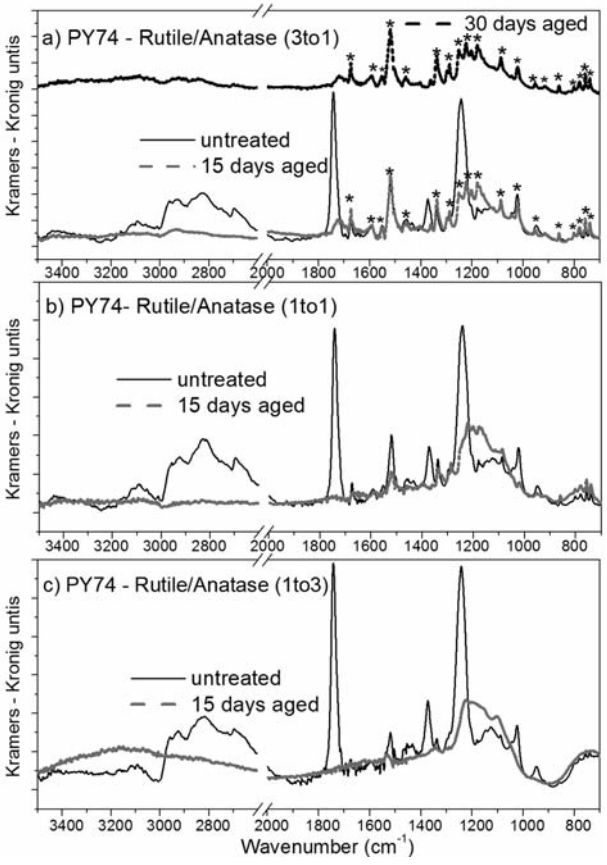

Figure 5: FT-IR reflectance spectra of paint layers of a) Hansa yellow PY74 (*) mixed with rutile/anatase in proportion 3 to 1; b) PY74 mixed with rutile/anatase in proportion 1 to 1; and c) PY74 mixed with rutile/anatase in proportion 1 to 3, before and after ageing.

erating the ageing process observed in the pure pigment layer.

Verdigris – pure or mixed with titanium dioxide – experimental tables were subjected to the influence of ultraviolet radiation and sulphur dioxide vapours at ambient conditions. In painting layers containing rutile the maximum in reflectance spectra / visible region is shifted from 500 nm to 525 nm already during the first three days. The reflectance values of paint layers containing rutile decrease between 400 and 600 nm, and increase at higher wavelengths (between 600 and 700nm) (Figure 6 a, b and d). In the same frame, Δa* and Δb* values greatly increase, while ΔL* is decreasing (Figure 7). In painting layers containing rutile/anatase alterations are much more significant, and the maximum is shifted from 500 nm to 625 nm already during the first three days, while after seven days a small increase in the violet region may be noticed. Reflectance values decrease in the green wavelength area, and increase in the yellow/red region (Figure 6 c, d). In the same frame, Δa* and Δa* values greatly increase, while ΔL* is decreasing (Figure 7).

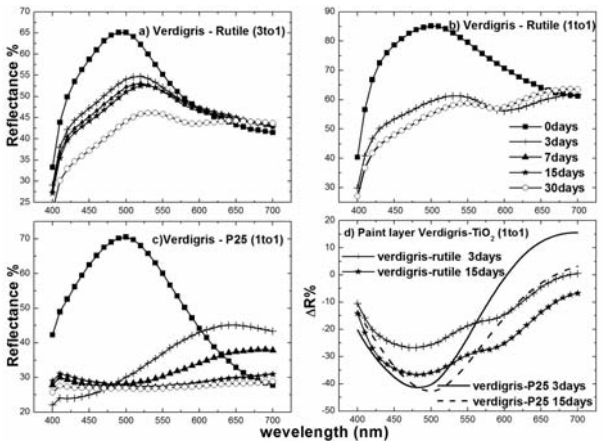

Figure 6: Reflectance spectra in visible region of untreated and artificially aged paint layers of a) Verdigris mixed with Rutile in proportion 3 to 1; b) Verdigris mixed with Rutile in proportion 1 to 1; c) Verdigris mixed with Rutile/Anatase in proportion 1 to 1; d) Reflectance spectra in visible region of artificially aged paint layers of verdigris mixed with TiO2 in proportion 1 to 1, reported as difference spectra ($\Delta R=R_{aged} - R_{untreated}$).

The colourant proved in all cases sensitive towards accelerated ageing, the colour change to a yellowish brown and finally dark grey hue being notably more pronounced in presence of rutile/anatase (Figure 8). In the FT infrared spectra all peaks corresponding to the poly(vinyl)acetate medium loose in intensity when subjected to the influence of intense external conditions, due to the decomposition of ester groups (1739, 1374 and 1243 cm^{-1}, Figure 9). In aged paint layer of verdigris-rutile/anatase the PVAc medium peaks are almost disappearing, and an important change is observed in the 1650-1250 cm^{-1} region (Figure 9 c). Since the region corresponds to acetate ion stretching bands, a significant change in the hydration state of copper acetate may be postulated. In fact, tenorite – CuO

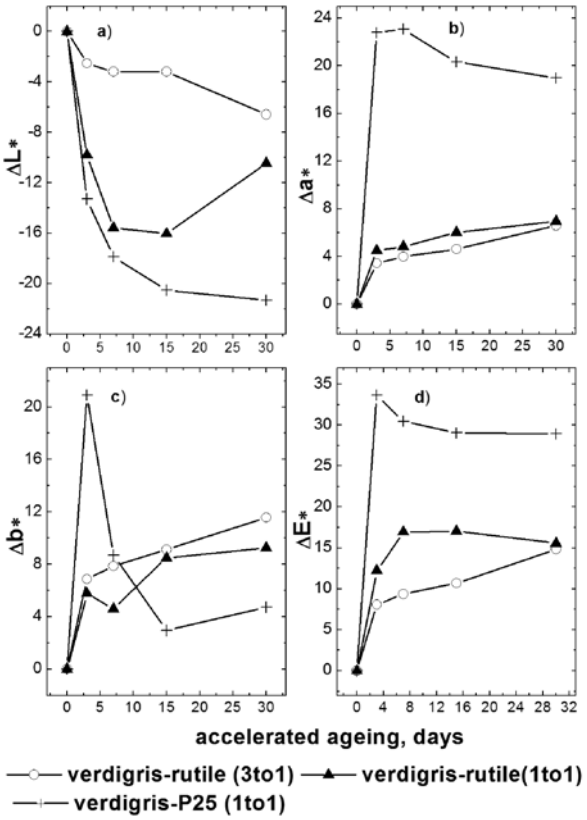

Figure 7 a) ΔL*, b) Δa*, c) Δb* and d) ΔE* changes of paint layers of verdigris and of verdigris mixed with TiO_2 during artificial ageing.

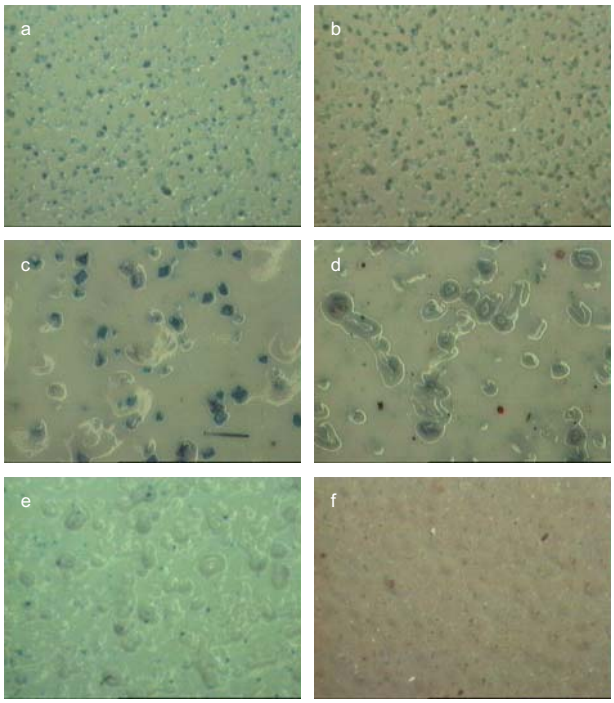

Figure 8: Surface photographs of verdigris paint layers; a: rutile 3:1, untreated; b: rutile 3:1, 15 days; c: rutile 1:1, untreated; d: rutile 1:1, 15 days; e: rutile/anatase 1:1, untreated; f: rutile/anatase 1:1, 15 days.

is formed under ageing conditions; while further reduction to cuprite – Cu_2O is accelerated by ultraviolet radiation.[25]

Although verdigris is sensitive to environmental influences under all circumstances, the results permit the assumption that the rutile form of titanium dioxide strongly protects the paint layer from degradation, while the rutile/anatase form (P25 Degussa) further accelerates the ageing process.

Recently, heterogeneous photocatalytic detoxification methodologies proved very promising for the treatment and disinfection of contaminated air. It is well established that initiation of photocatalytic degradation of paint layers containing TiO_2 is quite different from that of layers without TiO_2. Indeed, when a photon matches or exceeds the band-gap energy of TiO_2 particles, conduction-band electrons (e^-) and valence-band holes (h^+) are generated on the surface of TiO_2. Absorbed oxygen molecules can capture electrons, producing O_2^-, O•, O^- species. At the same time, photogenerated holes can be trapped by hydroxyl ions (OH^-) or water absorbed (H_2O_{abs}) on the surface, producing hydroxyl radicals (•OH), which play an important role in photocatalytic reactions.[19,20] The reactive oxygen species described above initiate the degradation reaction by attacking neighbouring polymer chains, and the degradation process spatially extends into the polymer through the diffusion of the reactive oxygen species. If the electrons and holes cannot be captured in time, they will recombine with each other within a few nanoseconds, and will reduce the photocatalytic efficiency of TiO_2.[20]

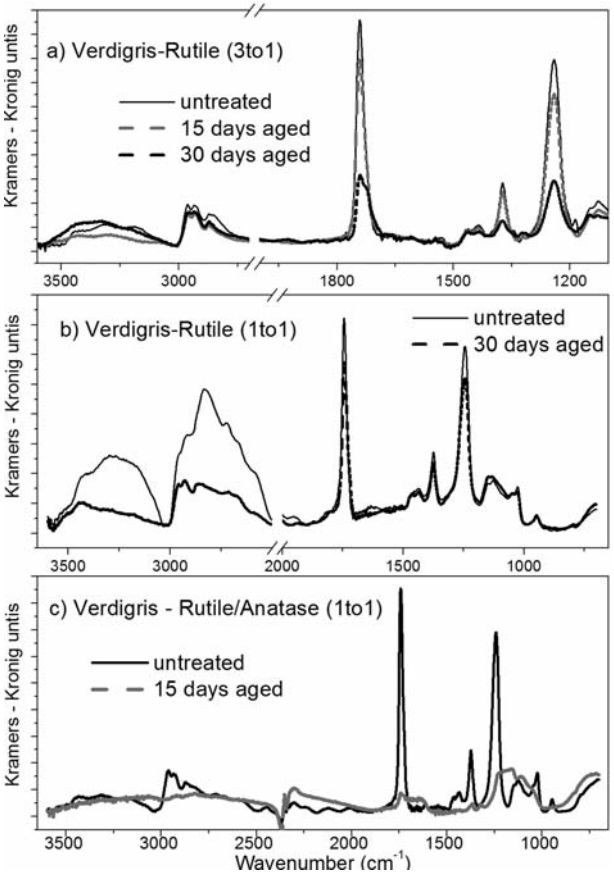

Figure 9: FT-IR reflectance spectra of paint layers of a) verdigris mixed with rutile in proportion 3 to 1; b) verdigris mixed with rutile in proportion 1 to 1; and c) verdigris mixed with rutile/anatase in proportion 1 to 1.

On the whole, addition of rutile/anatase is increasing the total colour difference ΔE* and enlarging molecular changes, hence paint layers containing this mixture are more susceptible to ageing. Thus, rutile/anatase (Degussa P25) shows greater photo-effectiveness than rutile. This has been attributed to three factors: (a) the rutile phase is acting as a transmitter extending photoactivity to longer wavelengths (rutile absorbs light at 410 nm, while anatase does at 385 nm); (b) the stabilisation of charge separation by electron transfer from rutile to anatase slows recombination; and (c) the small size of rutile crystallites facilitates this transfer, creating catalytic "hotspots" at the rutile-anatase interface.[21,26]

4 Conclusions

The role of titanium dioxide in the inherent protection of polychrome works of art is unambiguously depending on the type used. Thus, while photoactive rutile/anatase is accelerating ageing procedures, rutile – actually a typical pigment – is clearly protecting colourants placed in a contaminated and irradiated environment.

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6 References

1. P. Cox Crews, *The fading rates of some natural dyes*, Stud. Conserv., 1987, **32**, 65-72.

2. D.G. Duff, R.S. Sinclair, D. Stirling, *Light-induced colour changes of natural dyes*, Stud. Conserv., 1977, **22**, 161-169.

3. L.G. Salmon, G.R. Cass, *The fading of artist's colorants by exposure to atmospheric nitric acid*, Stud. Conserv., 1993, **38**, 73-91.

4. E. Kampasakali, Z.E. Papliaka, D. Christofilos, E.A. Varella, *The Russian Avant-Garde painting palette. Documentary and physico-chemical study of inorganic colorants*, Ann. Chim., 2007, **97**, 447-472.

5. M. Odlyha, N.S. Cohen, G.M. Foster, *Dosimetry of paintings: Determination of the degree of chemical change in museum*

exposed test paintings (smalt tempera) by Thermal Analysis, Thermochim. Acta, 2000, **365**, 35-44.

6. M. Odlyha, N.S. Cohen, R. Campana, G.M. Foster, *Determination of the degree of chemical change in museum exposed test paintings (lead white tempera) by Thermal Analysis*, Thermochim. Acta, 2000, **365**, 45-52.

7. M. Odlyha, N.S. Cohen, G.M. Foster, R.H. West, *Determination of the degree of chemical change in museum exposed test paintings (azurite tempera) by Thermal Analysis and Spectroscopic Analysis*, Thermochim. Acta, 2000, **365**, 53-63.

8. E. Marengo, M.C. Liparota, E. Robotti, M. Bobba, *Monitoring of paintings under exposure to UV light by ATR-FT IR spectroscopy and multivariate control charts*, Vib. Spectrosc., 2006, **40**, 225-234.

9. J. van der Weerd, A. van Loon. J.J. Boon, *FT IR Studies of the effect of pigments on the aging of oil*, Stud. Conserv., 2005, **50**, 3-22.

10. M. Bacci, M. Picillo, S. Porcinai, B. Radicati, *Evaluation of the museum environmental risk by means of tempera-painted dosimeters*, Thermochim. Acta, 2000, **365**, 25-34.

11. P. M. Whitemore, V. G. Colaluca, H. R. Morris, *The light bleaching of discoloured films of an acrylic artists' medium*, Stud. Conserv., 2002, **47**,228-236.

12. P. M. Whitemore, V. G. Colaluca, *The natural and accelerated ageing of an acrylic artists' medium*, Stud. Conserv., 1995, **40**, 1-64.

13. T. Learner, O. Chiantore, D. Scalarone, *Ageing studies of acrylic emulsion paints*, Preprints of the 13th Triennial meeting of the ICOM Committee for Conservation, Rio de Janeiro, 2002, 2, 911-919.

14. B. Ormsby, G. Foster, T. Learner, S. Ritchie, M. Schilling, *Improved controlled temperature and relative humidity DMA of artists' acrylic emulsion paint films, Part I*, J. Thermal Anal. Calorim., 2007, **90**, 249-253.

15. B. Ormsby, G. Foster, T. Learner, S. Ritchie, M. Schilling, *Improved controlled relative humidity denamic mechanical analysis of artists' acrylic emulsion paint films, Part II. General properties and accelerated ageing*, J. Thermal Anal. Calorim., 2007, **90**, 503-508.

16. D. Scalarone, O. Chiantore, T. Learner, *Ageing studies of acrylic emulsion paints. Part II*, ICOM Committee for Conservation 14th Triennial meeting, Preprints, James & James (Science Publishers) Ltd., The Hague, 2005, 350-317.

17. R. M. Johnson Feller, R. L. Feller, C. W. Bailie, M. Curran, *The kinetics of fading: Opaque paint films pigmented with alizarin lake and titanium dioxide*, J. Am. Inst. Conserv., 1984, **23**, 114-129.

18. R. L. Feller, R. M. Johnson Feller, C. Bailie, *Determination of the specific rate constant for the loss of a yellow intermediate during the fading of alizarin lake*, J. Am. Inst. Conserv., 1986, **25**, 65-72.

19. J. Shang, M. Chai, Y. Zhu, *Solid-phase photocatalitic degradation of polystyrene plastic with TiO_2 as photocatalyst*, J. Solid State Chem., 2003, **174**, 104-110.

20. J. Shang, M. Chai, Y. Zhu, *Photocatalytic degradation of polystyrene plastic under fluorescent light*, Environ. Sci. Technol., 2003, **37**, 4494-4499.

21. T. J Kemp, R. A Mclntyre, *Influence of transition metal – doped titanium(IV) dioxide on the photodegradation of polystyrene*, Pol. Degrad. Stability, 2006, **91**, 3010-3019.

22. A.J. Robinson, J. Wray, D.A. Worsley, *Effect of coloured pigmentation on titanium dioxide photo catalysed PVC degradation*, Mat. Sci. Technol., 2006, **22**, 1503-1508.

23. R. L. Feller, *Accelerated ageing, photochemical and thermal aspects*, The Getty Conservation Institute, Marina del Rey, California, 1994.

24. A. Whitaker, *Crystal structures of azo pigments derived from acetoacetanilide*, J. Soc. Dyers Colourists, 1988, **104**, 294-300.

25. M.R. Derrick, D. Stulik, J.M. Landry, *Infrared spectroscopy in conservation science*, The Getty Conservation Institute, Los Angeles, 1999.

26. D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh, M. C. Thurnauer, *Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO_2 using EPR*, J. Phys. Chem. B, 2003, **107**, 4545-4549.