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Characterization of photocatalytic paints: a relationship between the photocatalytic properties – release of nanoparticles and volatile organic compounds

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1 **Characterization of photocatalytic paints: A**
2 **relationship between the photocatalytic**
3 **property ó release of NanoParticles and Volatile**
4 **Organic Compounds.**

5
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21

22

23 ABSTRACT

24 Photocatalytic TiO₂ appears to be a promising method to eliminate many air pollutants such as
25 nitrogen oxides (NO_x) and volatile organic compounds (VOCs). However, number of questions
26 remain unanswered prior to their full optimization. Some photocatalytic materials are already
27 commercialized but their photocatalytic effects are questionable. In the present study, a
28 characterization of two paints for indoor and outdoor applications, one containing micro-size
29 titanium dioxide (TiO₂) particles and the other based on nano-TiO₂, is undertaken in order to
30 understand their environmental impact during the use phase. The photocatalytic efficiency of
31 the paints is determined before and after climatic ageing. The degradation of the paints induced
32 by their ageing was characterized in parallel. Powders, dispersions and paints applied on a
33 substrate are investigated to characterize the state of the NanoParticles (NPs) as a function of
34 their surrounding media. The abrasion of the photocatalytic materials indicates that the presence
35 of TiO₂ (NPs) enhances the organic matrix degradation of the paints due to a greater
36 photocatalytic effect. **The online and continuous measurements by PTR-ToF-MS indicate**
37 **that the degradation of the organic matrix leads to release of organic compounds**
38 **(formaldehyde, methanol, acetaldehyde and formic acid) in the air which suggests that**
39 **following only the removal of VOCs (in this case xylene) is not enough to make a proper**
40 **evaluation of the effectiveness of photocatalytic paints towards VOCs elimination. These**
41 **VOCs emerge exclusively from the degradation of the organic matrix as much lower**
42 **VOCs emissions were measured in the case of the aged paint which exhibits a lower**
43 **amount of organic composition in the matrix.** This study links the morphological
44 observations, chemical determination, structural parameters and photocatalytic properties of the
45 paints for future optimization of a safer-by-design photocatalytic paints.

46

47

48 INTRODUCTION

49 In the construction industry, nanotechnology creates the possibility to produce materials with
50 novel functionalities and improved characteristics. Products containing nanomaterials (NMs)
51 have been developed for the construction sector¹ (cement, wet mortar and concrete, paints,
52 coatings, insulation materials, glass²) because of their enhanced properties such as higher
53 durability, fire resistance, thermal stability, self-cleaning and photocatalytic properties.
54 Engineered Nanoparticles (ENPs), which by convention mean objects having at least one
55 dimension within the nanometer range (1-100 nm), are more and more used in industrial
56 applications. Different types of NPs are added in commercial paints to improve for instance
57 their mechanical properties (SiO₂)², their UV resistance³, their rheological properties⁴ or to
58 modify their coloring⁵. The industry associated with production of NPs takes into consideration
59 a responsible development of its products⁶. This requires in particular a control of the NPs
60 throughout the life cycle of the product. In this context, many toxicity studies are devoted to
61 properly assess the impact of different types of NPs and their surrounding matrix, on human
62 health⁷. Nevertheless, the best way to prevent inhalation and ingestion of NPs but also to avoid
63 dermal contamination is to protect workers and consumers with appropriate equipment or to
64 reduce the release of NPs in the environment. Therefore, some studies are more focused on the
65 risk protection by studying collective^{8,9} and personal¹⁰⁻¹³ protection systems while other studies
66 investigate all the ways leading to reduce the release of the nanoparticles while maintaining
67 their initial property (photocatalytic, antibacterial, reinforcement...) ^{14, 15}.

68 A paint is generally composed of different components as binders, fillers, pigments, solvents,
69 diluents and different additives like dispersing, thickeners and antifoam. The polymeric binder
70 brings the adhesion to the substrate and the chemical resistance of the paint, fillers reduce cost
71 and enhance the physical properties of paints and pigments provide the coloring to the paint.
72 Titanium dioxide (TiO₂) particles with a micro-size are usually used as white pigment in paints.

73 When TiO₂ with nano-range size are embedded in the paint, the coloring property is lost but
74 these NPs provide a photocatalytic effect reducing air contaminants such as NO_x and VOCs in
75 the environment to indoor and outdoor construction materials¹⁶⁻¹⁹ (concrete, asphalt, tiles,
76 paints). Regarding the outdoor applications, the TiO₂ NPs were used to attempt to reduce the
77 adverse effects of urban air pollution on human health. Titanium dioxide (TiO₂) based
78 photocatalytic surfaces have been tested, both, at a laboratory scale and in the real-life urban
79 environment for the remediation of Nitrogen Oxides (NO_x), Volatile Organic Compounds
80 (VOCs) Ozone (O₃) and atmospheric particles. The results of these studies are controversial
81 and the reasons for these contradictory results are still under discussion suggesting that further
82 studies are necessary in order to accurately determine the impact of photocatalytic materials on
83 air quality. Few studies have demonstrated that instead of VOCs elimination, the emission of
84 carbonyl compounds occurs during the irradiation of the photocatalytic paints. For example,
85 **Gunschera *et al.*²⁰ identified emissions from building materials as formaldehyde, furfural,**
86 **acetophenone, n-butylbutyrate, n-butyl-i-butyrate, n-butylpropionate, 4-heptanone,**
87 **acetic acid, i-butyraldehyde and crotonaldehyde, in the case of photocatalytic tiles.** The
88 release of harmful aldehydes such as formaldehyde, acetaldehyde, 2-ethylacrylaldehyde,
89 pentanaldehyde, and hexanaldehyde was observed upon irradiation of photocatalytic paints²¹.
90 Another controversial issue is the potential formation of by-products such as nitrous acid
91 (HONO)²², which is even more harmful than the primary reactants NO and NO₂. Regarding the
92 indoor application of photocatalytic paints, Gandolfo *et al.*²³ have shown that HONO is released
93 in the indoor air in function of the embedded quantity of TiO₂ nanoparticles.
94 In parallel, other studies are more focused on the possible release of TiO₂ NPs in the
95 environment during the use phase of the photocatalytic paints. Al Kattan *et al.*²⁴⁻²⁵ studied the
96 TiO₂ NPs release from paints before and after climatic ageing and also their behavior when
97 exposed to different media (pH and different organic matters). Olabarrieta *et al.*²⁶ immersed the

98 photocatalytic paints in different media during UV irradiation. Shandilya *et al.*²⁷ investigated
99 the emission of TiO₂ NPs during ageing in water with the analysis of the run-off and in the air
100 via abrasion experiments. All stated that the photocatalytic effect initiated by UV-light degrades
101 the organic matrix of the paints and increases the release of NPs to the environment.

102 The present paper links both NPs and VOCs release in the environment during the ageing of a
103 photocatalytic paint. The aim of the study consists in a better understanding of the main
104 parameters controlling the release of NPs from nanomaterials in order to formulate, in the
105 future, safer-by-design paints i.e. less NPs and VOCs releasing paints with the same
106 photocatalytic efficiency. For this purpose, two different paints were investigated. Both paints
107 exhibit the same formulation, but they differ by the amount and size (micro and nano) of the
108 TiO₂ particles. The paint containing micro-TiO₂ is already commercialized, and the one with
109 the nano-TiO₂ is still under development. The use phase of these two products was investigated
110 by simulating environmental and mechanical ageing.

111 TiO₂ powders, dispersions and paints applied on a substrate were characterized to determine
112 the chemical nature, the particle size distribution, the particle shape and the dispersion state. In
113 a second phase, outdoor ageing of the products was simulated: painted panels were exposed to
114 accelerated weathering. The photocatalysis property of TiO₂ powders and applied paints was
115 investigated by EPR (Electron Paramagnetic Resonance) and the photocatalytic activity was
116 measured with an HR PTR ToF MS (High Resolution Proton Transfer Reaction Time of Flight
117 Mass Spectrometry) before and after ageing to correlate with the surface characterization. All
118 these technics allowed to perform the analysis of the surface and the bulk of each sample. It
119 facilitated the understanding of the weathering effect on paints, of its impact on NPs release
120 and on the interaction between the polymeric binder and pigments. Abrasion tests were
121 performed with a Taber abraser to simulate a mechanically induced ageing.

122

123 MATERIALS AND METHODS

124 **Preparation of the paints**

125 **All the analyzed samples were provided by the same manufacturer ALLIOS. Two types**
126 **of paints were investigated. Both paints were composed of the same constituents in the**
127 **same proportion such as an acrylic-based binder, inactive microsize TiO₂ for the white**
128 **color, calcium carbonate particles, aluminosilicate, water and other additives, called**
129 **õbasic paintö. Their formulation differed only by the size of TiO₂ particles used. For the**
130 **formulation of the photocatalytic paint, a slurry was at first made. The D2 slurry was**
131 **composed of TiO₂ NPs called P2 in anatase form and the D1 slurry was composed of**
132 **inactive TiO₂ microsize particles called P1. Both slurries D1 and D2 contained of about**
133 **70% (w/w) of P1 and P2 TiO₂ respectively in water. About 5% (w/w) of D1 and D2 slurries**
134 **were mixed with the õbasic paintö to reach 2.5% (w/w) of P1 and P2 in PM1 paint (for**
135 **Matte Paint 1) and PM2 paint (Matte Paint 2). PM1 and PM2 were both investigated to**
136 **compare a non-reactive paint with a reactive one. The manufacturer provided powders,**
137 **dispersions, liquid paints and also paints applied on different substrates allowing us to perform**
138 **various experiments and characterizations.**

139 TiO₂ powders (P1 and P2) were characterized by X-Ray Diffraction (XRD, Bruker-advance
140 diffractometer), by Scanning Electron Microscopy coupled with an Energy Dispersive X-ray
141 spectrometer (SEM-EDX, LEO Electron Microscopy Ltd, Quantas EDX, Bruker Nano), by
142 Transmission Electron Microscopy coupled with an Energy Dispersive X-ray spectrometer
143 (TEM-EDS, FEI Tecnai Osiris) and by X-Ray Photoelectron Spectroscopy (XPS, PHI Versa
144 Probe II spectrometer). As the P2 NPs are agglomerated in the powder state, they were
145 characterized in solution by cryo high resolution-transmission electron microscopy (cryo HR-
146 TEM, FEI Tecnai Osiris). Dispersions D1 composed of about 70 weight % of P1 microparticles
147 in water and dispersion D2 composed of about 70 weight % of P2 nanoparticles in water were

148 also investigated since the manufacturer use these dispersions to formulate the paints. Small-
149 Angle X-Ray Scattering (SAXS) and Small-Angle Neutron Scattering (SANS) were used to
150 determine the real size and the structure of the P2 NPs in the dispersed state. These techniques
151 were chosen because they provide results which are more representative of the samples
152 compared to TEM observations. Paints applied on Leneta plastic substrates (black plastic-vinyl
153 chloride/acetate copolymer with smooth matte surface, thickness of 0.25 mm and size of 165 x
154 432 mm) were characterized by SEM-EDS and XPS before and after accelerated weathering.
155 The photocatalytic property was measured by EPR (EMX Bruker spectrometer) on powders
156 and applied paints under solar simulation (New Port Oriel, Sol 3A class AAA solar simulator
157 94023A). A Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-ToF-MS)
158 (Ionicon) was connected to a sealed reactor during the injection of a VOC on painted surfaces
159 stored during 21 days in an oven ventilated by clean air at 23°C and 55 % relative before to
160 evaluate their photocatalytic efficiency with respect to xylene. Paints applied on metallic
161 substrates (Taber industries aluminum panels of 100mm² with a 6.35 mm center hole) were
162 used for abrasion tests (Taber Abraser (type 5131, Taber Industries) before and after accelerated
163 weathering in a QUV climatic chamber (Q-Lab, USA).

164

165 **Photocatalytic efficiency.**

166 The photocatalytic effect was measured before and after accelerated weathering of both paints.
167 For these measurements, paint samples are placed in a flow tube reactor and exposed to VOCs.
168 For details about the working principle of the flow tube reactor the readers are referred to
169 Gandolfo *et al.*^{19, 23}. The flow tube reactor is coupled to a PTR-ToF-MS for on-line and
170 continuous measurements of the variations of the concentrations of VOCs. This system is very
171 sensitive for real-time monitoring of VOCs present in the air (acetone, acetaldehyde, methanol,
172 ethanol, benzene, toluene, xylene among the others). Two types of experiments were conducted,

173 (i) following the concentrations of all the released VOCs from the samples upon light irradiation
174 and (ii) following the removal of one selected VOCs (xylene) due to the photocatalytic
175 efficiency of the paint. We have chosen to monitor the elimination of xylene by photocatalytic
176 paints because it is considered toxic for humans²⁸, it is not emitted in the air by paints and it is
177 present in non-negligible concentrations in indoor atmospheres²⁹ because some materials
178 generate this compound³⁰.

179

180 **Photocatalytic property measured by EPR.** EPR spectra were obtained at 9 GHz at room
181 temperature. Samples were observed either wetted or with pure 5,5-dimethyl-1-pyrroline N-
182 oxide (DMPO) used as spin trap. It consists in trapping radicals that are extremely difficult
183 to be observed because of their short life time, by a diamagnetic molecule in order to obtain a
184 stable paramagnetic species. The spin trapping technique involves the addition of the unstable
185 radical to the double bond of a diamagnetic spin trap. This technique allows the identification
186 of the nature of the unstable trapped radical. Such analyses were performed in dark or under 15
187 min light irradiation with a solar simulator to characterize the photocatalytic property of the
188 paints. For irradiation tests, samples were placed in a fixed position located at 5 cm below the
189 device producing the photons from the solar simulator. In this way, the center of the solar
190 simulator coincide with the center of the sample. The EPR spectra were recorded under Ar
191 atmosphere after air exchange inside a glovebox in order to avoid broadening of the line widths
192 due to the presence of oxygen.

193

194 **Ageing: Q-UV exposure conditions.** Paint coated panels (Leneta and aluminum) were exposed
195 to UV lamps in an accelerated weathering chamber for 500 hrs according to the ISO norm
196 16474-3:2013 (ISO 2013). The applied lamp is a Fluorescent UVB 313 and the UV light was
197 emitted in the wavelengths range from 290 nm to 400 nm with a maximum applied irradiance

198 of 0.71 W m⁻² at 310 nm. Paints underwent two different cycles: a) 5hrs with lamps switched on
199 at a temperature of 50±2 °C and b) 1hr with lamps switched off with a water spray at a
200 temperature of 25±2 °C. Exposed paints to UV lamps were noted as QUV. The total radiance
201 exposure was 1.44 MJ m⁻² giving a maximum acceleration using short wavelength UV.

202

203 **X-Ray Diffraction (XRD).** The crystallographic structure of nanoparticles was investigated
204 using a Bruker-advance diffractometer in geometry θ -2 θ , equipped with a Cu-K α source and a
205 LynxEye linear detector. θ -2 θ patterns were achieved in order to identify the various
206 crystallographic phases and precisely measure their lattice parameters.

207

208 **Small-angle scattering:** Small-Angle Neutron Scattering (SANS) experiments were performed
209 on the D22 spectrometer of the Institut Laue-Langevin (ILL, Grenoble). Three different
210 configurations (incident wavelength, λ and sample-to-detector distance) were used to cover a
211 transfer momentum range from $3 \cdot 10^{-3}$ and 0.5 \AA^{-1} , q (where $q=4\pi \sin \theta/\lambda$ and θ is the scattering
212 angle). Small-Angle X-ray Scattering (SAXS) experiments were performed on the D2AM
213 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble). Both dispersions
214 D1 and D2 were studied in liquid cells with quartz and Kapton windows for SANS and SAXS,
215 respectively. Usual corrections for intensity normalization and background subtraction were
216 applied³¹.

217

218 **Scanning Electron Microscopy coupled with an Energy Dispersive X-ray Spectrometer**
219 **(SEM-EDS).** Images were acquired with an ultra-High Resolution SEM (HR-SEM). Samples
220 were covered by a 10nm layer of platinum to prevent charging during observations. For the
221 acquisition of images, the working distance was less than 4mm with an accelerating voltage of
222 5kV and a diaphragm of 30 μ m. EDS analysis were performed to obtain chemical information

223 on observed samples. The quantification of EDS spectra was done using the δ ESPRIT δ
224 software, allowing an accurate chemical elemental analysis. For this, the working distance and
225 the accelerating voltage were raised to 8mm and 15kV respectively, with a diaphragm of 60 μ m.
226 SEM-EDS allowed us to characterize powders and paint samples applied on Leneta substrates
227 before and after ageing.

228

229 **Transmission Electron Microscopy coupled with an Energy Dispersive X-ray**
230 **Spectrometer (TEM-EDS).** TEM samples were prepared by simple drying of a drop of the
231 sonicated solution on a carbon film grid. This analytical system owns four EDX detector giving
232 a solid angle close to 1 steradian. Analysis were carried out in STEM mode using the HAADF
233 (High Angle Annular Dark Field) detector at a high voltage of 200 kV with a probe current of
234 0.4 nA. Probe size was approximately 5 angstrom. Cryo-preparation was carried out using a
235 Vitrobot plunger in liquid ethane. After sonication, a drop of the solution was deposited on a C-
236 FLAT carbon grid and freeze at ethane temperature. Observations were made using a single tilt
237 Gatan cryo holder working at liquid nitrogen temperature. Images were recorded using low-
238 dose mode at 200 kV (dose reduced to 10 e \cdot A.s $^{-1}$) with a Gatan BM-Ultrascan camera
239 equipped with a biological scintillator.

240

241 **X-Ray Photoelectron Spectroscopy (XPS).** XPS allowed us to determine the surrounding
242 environment of elements present at the near surface of samples (first 10 nm).The XPS
243 measurements were performed using spectrometer with a monochromatized Al K X-ray
244 source (1486.6 eV) focalized to a spot of 100 μ m and with an electron take-off angle of $\theta =$
245 45 $^\circ$. Survey spectra were recorded with a pass energy of 117 eV and the high-resolution spectra
246 were registered with a pass energy of 23.5 eV. Known as non-destructive surface analysis

247 instrument, XPS allowed us to probe the chemical bonds and their evolution after climatic
248 ageing.

249

250 **Abrasion process.** All manipulations were performed in a so-called low noise glove box
251 equipped with an HEPA filter in order to limit the initial presence of particles in the
252 atmosphere³². The background noise in the sealed glove box was quantified by a Condensation
253 Particle Counter (CPC) to be less than 5 particles cm⁻³. This particular condition was achieved
254 by creating a vacuum which sucks the air at a rate of 150 l min⁻¹ at the top of the box. A clean
255 air was obtained using a filter placed at the bottom of the glove box. For the abrasion of the
256 surface paints, a Taber Abraser was used. This test simulated the ageing effect induced by a
257 mechanical friction. A S42 abrasive sticker paper was set on CS-0 wheel to simulate the sanding
258 process of a surface. A weight of 500g was applied on both wheels of the Taber during 100
259 cycles of rotary abrasion at 60rpm. These abrasion conditions are conforming the standard ISO
260 7784-2 (ISO 2006).

261 The characterization of the released particles due to the abrasion process was obtained by the
262 determination of the particle size distribution with an Electrical Low Pressure Impactor (ELPI)
263 (DEKATI ltd, Tampere, Finland). The ELPI allowed to collect aerosolized particles according
264 to their aerodynamic diameter on hydrophilic polycarbonate membranes containing holes of
265 100 nm. Both membranes located in the two last impactor stages of the ELPI column,
266 corresponding to the smallest particles size impaction (of about 10nm), were then analyzed by
267 SEM-EDS. The goal was to observe the morphology and the size, and also to determine the
268 elemental analysis of the collected nanoparticles.

269

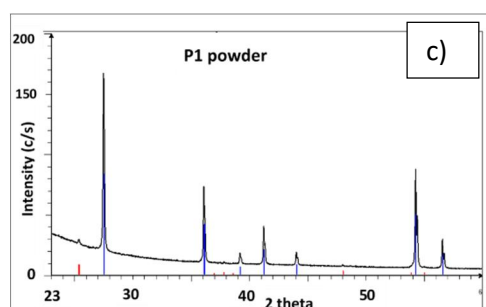
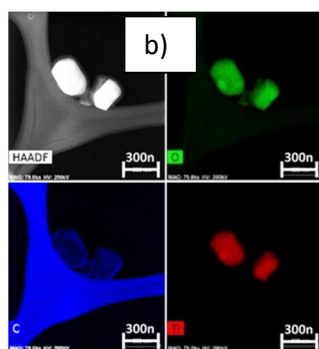
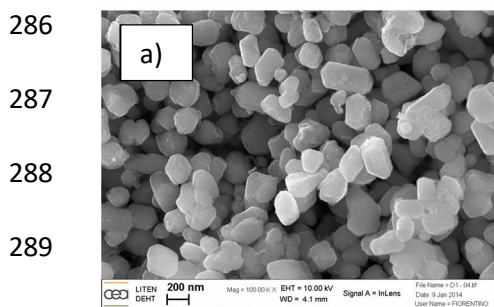
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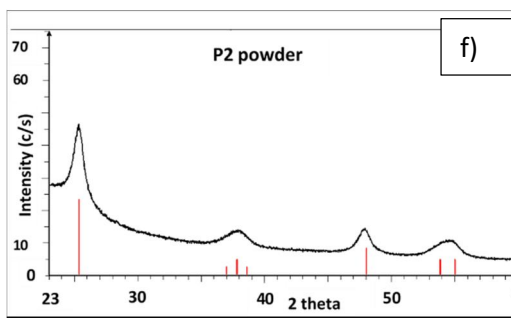
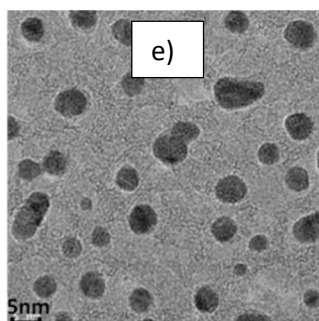
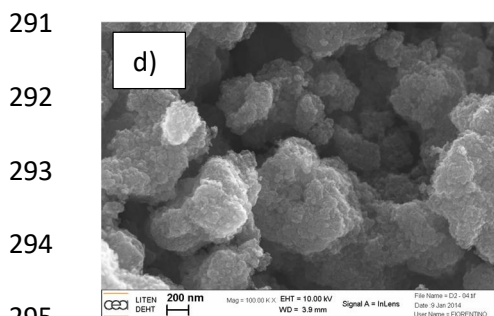
272 RESULTS

273 **Characterization of pristine particles P1 and P2.** Pristine particles were observed by
274 microscopy (SEM and TEM), chemical identification was conducted by EDS and their
275 crystalline structure were determined by XRD. As seen on Figure 1, particles P1 had an
276 elongated shape and their size was of about 240nm in length and 150nm in width. P2 particles
277 were aggregated, forming pellets with size above 200nm as observed by SEM. TEM-EDS
278 observations show that P1 particles were coated with a thin layer of carbon. To better observe
279 P2 NPs, a cryo-HR-TEM was used to observe a solution composed of P2 NPs and water in a
280 frozen state. Isolated NPs with an average diameter of about 5nm were observed.
281 EDS measurements identified predominantly titanium and oxygen for both powders. XRD
282 measurements reveal that P1 is mainly composed of particles having a rutile crystalline
283 structure and a minor crystallite structure anatase phase. On the other hand, P2 has only an
284 anatase crystalline structure.

285



290



295

296 Figure 1: a) SEM micrograph, b) TEM micrograph, c) XRD measurement of pristine P1
297 microparticles. d) SEM micrograph, b) HR cryo-TEM micrograph, c) XRD measurement of
298 pristine P2 nanoparticles.

299

300 **Characterization of P1 and P2 dispersions:** The structure of P1 and P2 dispersions were
301 studied by SANS and SAXS. The spectra are presented on Figure 2. A scaling factor, the same
302 for both P1 and P2, was applied to the SAXS data to superimpose with SANS results. The
303 scattered intensity varies over 8 orders of magnitudes. The spectra obtained with the D1 and
304 D2 dispersions are very different on the overall angular range. The D1 spectra vary as q^{-4} as
305 expected for large size particles according to the Porod's law. The deviation observed at large
306 angles is significant and cannot be eliminated, modifying the background subtraction. The D2
307 spectra appear strongly different with a q^{-3} upturn in intensity at low angles, characteristic of
308 aggregated particles with a strong dispersion in the aggregation number and an oscillation
309 around 0.1 \AA^{-1} that should originate from particles with a size around 5nm. The SANS and
310 SAXS data for both dispersions are exactly superimposable at low angles. The contrast for X-
311 rays is directly related to the very large electron density difference of TiO_2 compared to water
312 while Ti presents a negative scattering length enhancing the contribution of a carbon shell. But
313 interestingly, the spectra do not match anymore at large angles, revealing a non-homogeneous
314 structure. Based on the characterization results presented above, the spectra were fitted with a
315 core-shell model assuming spherical particles with a TiO_2 core surrounded by a thin carbon
316 shell for calculating the scattering length densities with a Gaussian polydispersity of 0.35. The
317 same particle core diameter and shell thickness were used to adjust the SAXS and SANS
318 spectra. For D1, a value of 150nm was chosen for the core radius because this value cannot be
319 adjusted due to the large size of the particles. The shell thickness is 0.6 nm. For D2, the core
320 radius is 1.2nm and the shell was found to be very thin (0.16nm) which indicates that it cannot

321 be undoubtedly identified by TEM or XPS characterizations. The possible reason for this could
322 be the carbon contamination of the TiO₂ NPs. The signal scattered at low angles for D2
323 originates from aggregated particles with a fractal structure, the contribution of which is not
324 encountered in the model. Comparing the level of intensities between the upturn in intensity
325 and form factor of the nanoparticles, it can be estimated that less than 10% of the nanoparticles
326 are aggregated in agreement with cryo-TEM observations in Figure 1e).

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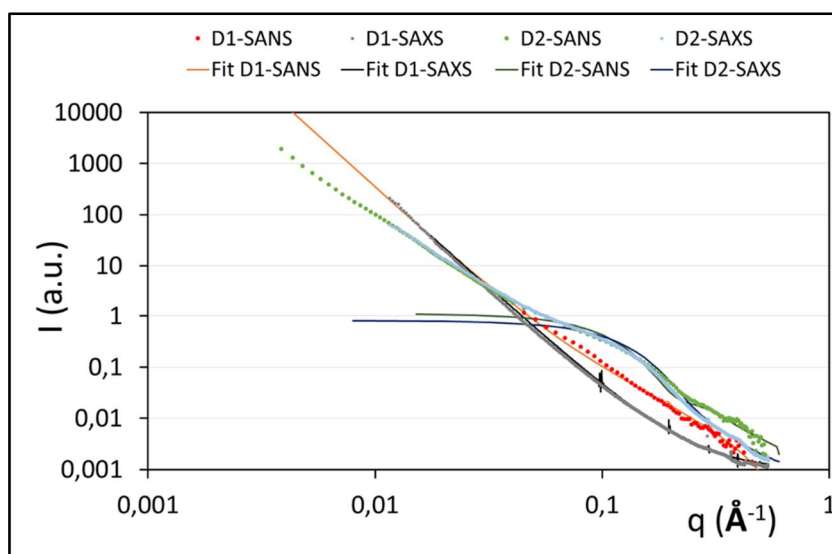
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336 Figure 2: SANS and SAXS profiles of D1 and D2 dispersions as a function of the scattering-
337 vector modulus q and their respective theoretical simulations.

338

339 **Surface characterization of applied paints PM1 and PM2 before and after ageing.** PM1

340 and PM2 were applied on Leneta substrate (polymer substrates). SEM images of the paints

341 surface before and after the QUV ageing are shown in Figure 3 at different scales (X1000,

342 X10000, X100000). At each scale, differences were observed between aged and non-aged

343 paints. By focusing at the largest scale (X100 000) before ageing, it could be seen that P1 and

344 P2 particles were covered by a thin layer of organic matrix. After ageing, the organic layer had

345 disappeared, P1 and P2 were found at the surface of samples. For PM1, a dense layer of P1 is

346 observed after ageing. In the case of PM2 sample, not only P2 particles, but also the plastic
347 substrate, was observed at the surface.

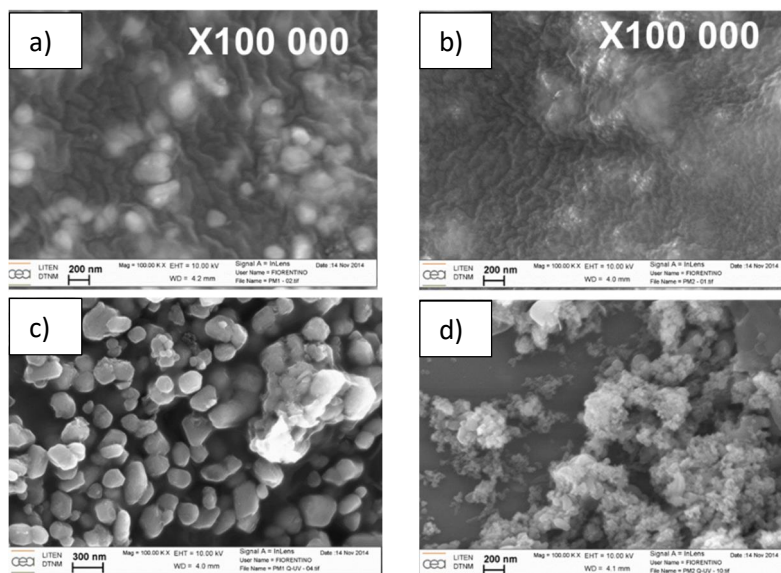
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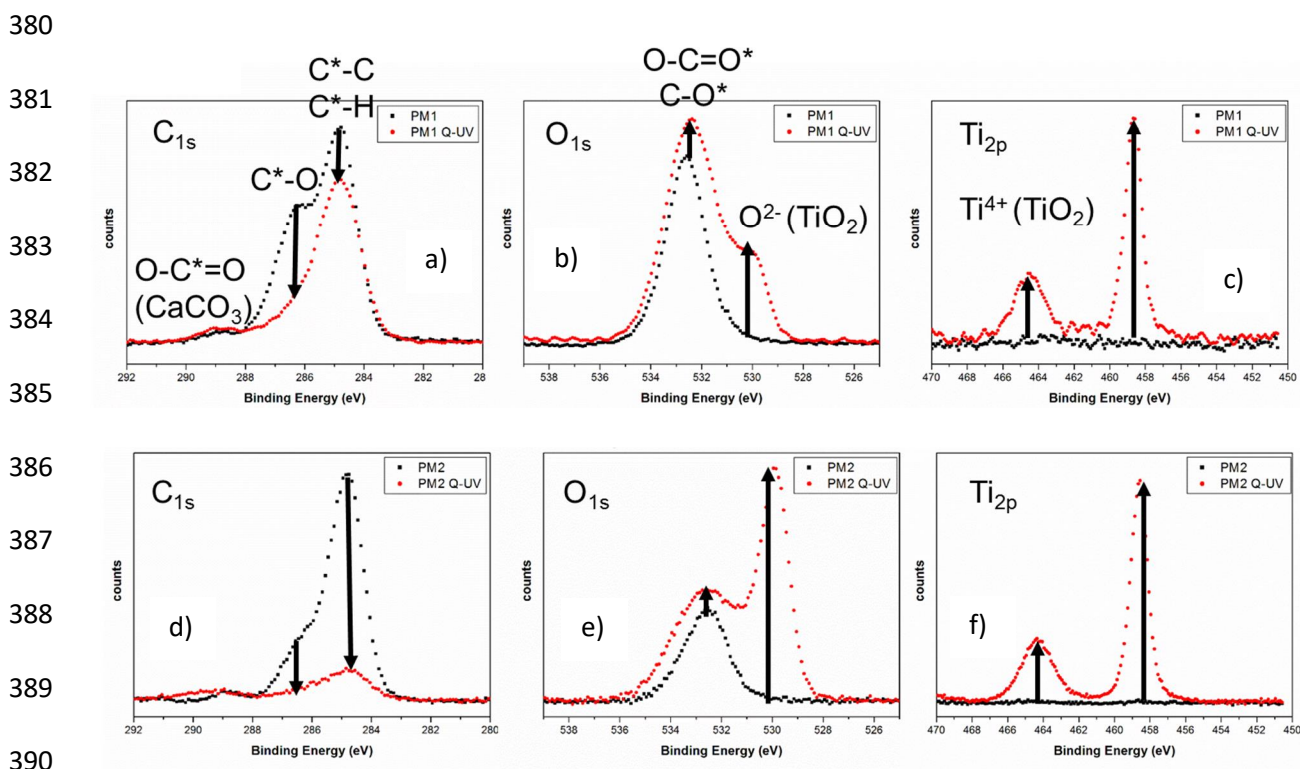
357 Figure 3: SEM images of a) PM1, c) PM1 Q-UV, b) PM2, d) PM2 Q-UV at X100 000 scale.

358

359 To better understand the effects emerging from the ageing of both paints, XPS measurements
360 were performed before and after ageing (Figure 4). The XPS C 1s core peak registered at the
361 surface of PM1 and PM2 samples before ageing (in black on Figure 4) was the signature of
362 species related to the organic matrix for instance C-C/C-H at (284.8 eV), C-O at (286.3 eV),
363 COO at (289.0 eV) and CO₃ bonds related to CaCO₃. The O 1s core peak corroborated this
364 effect by the presence of a main peak at (532.4 eV) related to acrylic and vinyl copolymer. The
365 Ti 2p core peak was not detected before ageing in the case of both paints, indicating that the
366 organic layer (observed by SEM on Figure 1) covering the surface of TiO₂ particles was thicker
367 than 5 nm.

368 After ageing (in red on Figure 4), the intensity of the C-O and C-C related peaks at the C 1s
369 peak decreased and simultaneously the O 1s showed the appearance of a shoulder at 530 eV

370 assigned to TiO₂ particles. The valence state of TiO₂ particles was probed by the mean of Ti 2p
 371 peak indicating the presence of +4 oxidation state of titanium (peak at 458.6 eV).
 372 In the case of PM2 paint, qualitatively a similar behavior was observed. However, some
 373 differences were observed quantitatively. Before ageing, the amount of C-O was lower .The
 374 ratio O [O²⁻]/O[organic] before and after UV exposure was evaluated for both samples, and
 375 reported to be 0 and 0.42 in the case of PM1 and 0 and 2.08 for PM2 sample.
 376 In the case of PM2 paint, the higher intensity of Ti⁴⁺ and of O²⁻ peaks registered after ageing
 377 was related to the presence of mainly P2 TiO₂ nanoparticles at the extreme surface of the
 378 sample. In parallel, the polymer matrix degradation was observed with the decrease of the C-
 379 O-related peak of the C1s spectrum.

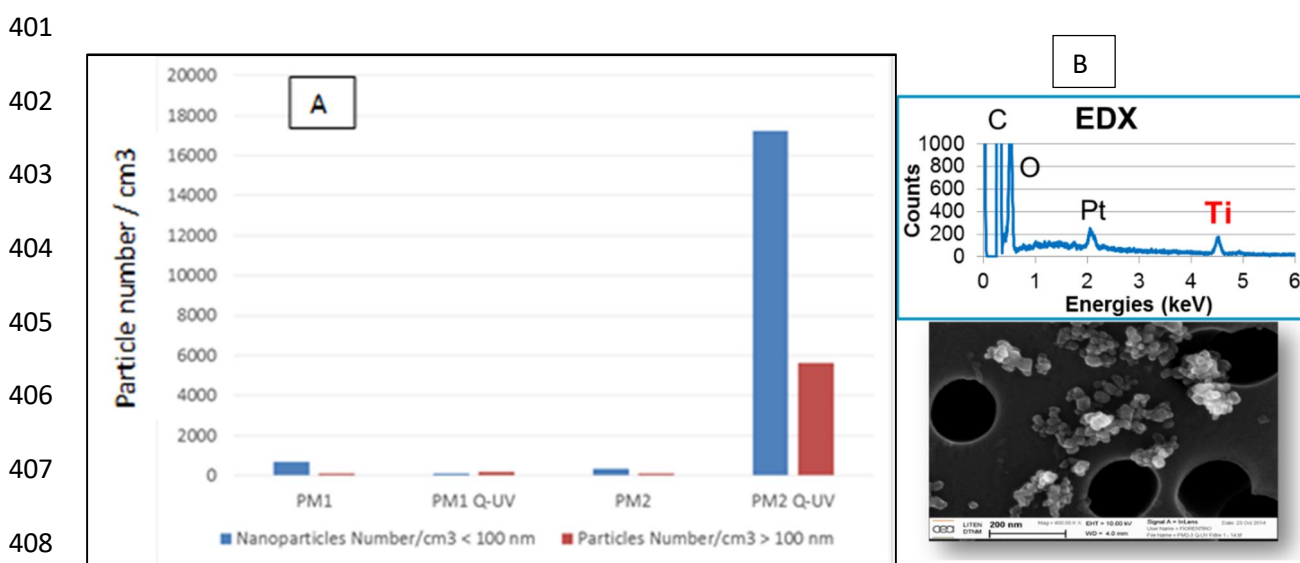


391 Figure 4: XPS spectra of PM1 and PM2 before and after ageing. a) C1s, b) O1s, c) Ti2p core
 392 level spectra of PM1 and d) C1s, e) O1s, f) Ti2p core level spectra of PM2.

393

394 **Aerosolized particles characterization.** Particle size distributions analyzed by ELPI counter
395 during ongoing abrasion process are depicted in Figure 5. This type of counter measured the
396 particle diameter as a function of their aerodynamic diameter (ranging from 7 nm to 10 μm). It
397 was observed that all the non-aged paints released less particles than the aged paint containing
398 nanoTiO₂ (PM2).

399 Aged PM2 sample released mostly NPs with diameter smaller than 100nm. NPs impacted on
400 the last stage of the ELPI column were observed by SEM-EDX and were found to be TiO₂ NPs.



409 Figure 5: A) Concentration of particles released as a function of the particle size measured with
410 ELPI; B) SEM-EDS characterization of the released particles.

411

412 **Test of the photocatalytic performance.** Signals provided by both powders with and without
413 solar simulation have been recorded and are gathered in Figure 6a). Since the considered
414 photocatalytic paints in this study absorb in the visible range of wavelengths, even in absence
415 of solar light irradiation (only presence of ambient light), both TiO₂ powders give EPR signals.
416 The light irradiance supplied by the lamps present in the room is sufficient to shift the electron
417 of the valence band towards the conduction band forming an electronic dipole (electron /
418 electron hole). The electron (e⁻) and the electronic hole (h⁺) react with gas, such as molecular

419 oxygen (O_2) and water vapor (H_2O) adsorbed on the semiconductor surface (TiO_2). The
420 formation of these hole-electron pairs creates highly reactive species such as hydroxyl radicals
421 ($\cdot OH$), superoxide radical ($\cdot O_2^-$) and hydrogen peroxide radical ($\cdot OOH$) that oxidize organic
422 compounds which are adsorbed on the surface of the catalyst³³. The EPR signal is composed of
423 three lines with respective g-factor of 2.023, 2.009 and 2.004 which can be interpreted in two
424 ways: either to the $Ti^{4+}O_2^-Ti^{4+}OH\cdot$ species³⁴⁻³⁸ or to oxygenated radicals³⁹ due to photoreaction
425 of residual organic groups as reported for cysteine-modified TiO_2 colloids^{37, 40} ascribed to TiO_2
426 reactivity. The broad signal observed at higher g-value (between 2.08 and 2.06) may be likely
427 ascribed to $\cdot O_2^-$ adsorbed on the nanoparticle surface⁴¹. At lower g value ($g=1.96$), we did not
428 observe the signal corresponding to electrons⁴², which could possibly be attributed to the
429 difference between the temperature of observation, 10K in our case against 4K in the study by
430 Kumar *et al.*⁴². Both signals of nano and micro TiO_2 particles spectra look very similar, except
431 for the first line (higher g value) for micro TiO_2 which appears at slightly higher g-factor
432 compared to nano TiO_2 (2.035 against 2.026)⁴². Under solar simulation, signals are more intense
433 for both powders. However, nano TiO_2 powder was the most reactive (in dashed grey line) and
434 showed higher intensity signals.

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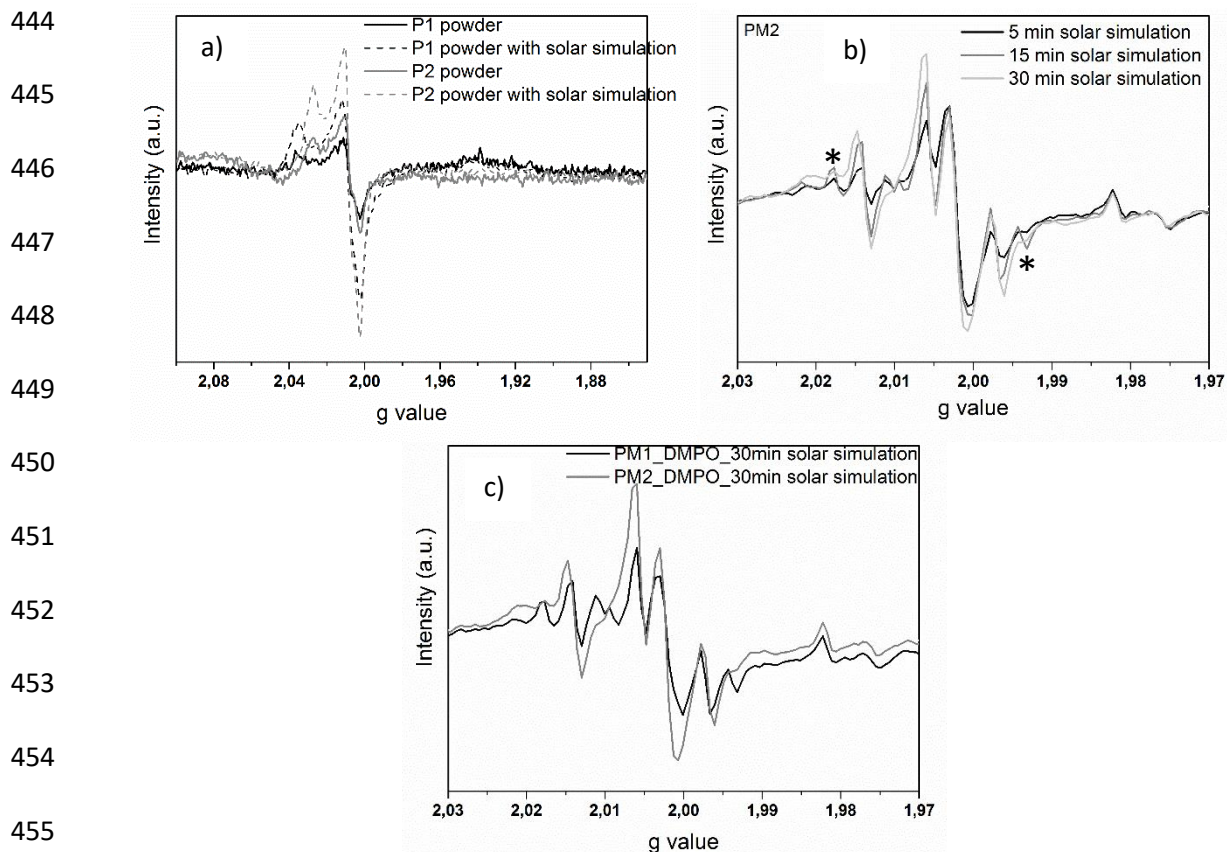
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456 Figure 6: EPR signals of a) microTiO₂ P1 and nanoTiO₂ P2 powders with and without solar
 457 irradiation, b) PM2 paint applied on Leneta substrates with DMPO in function of the duration
 458 of the solar irradiation and c) PM1 and PM2 applied on Leneta substrate with DMPO both after
 459 30min of solar irradiation.

460
 461
 462 EPR experiments were also conducted on paints applied on Leneta substrates in the presence
 463 and absence of solar irradiation, Figure 6b and c). In order to observe the various radical species
 464 involved during the TiO₂ catalysis photoreaction, we have applied the so-called spin trapping
 465 method. The unstable free radical reacts with DMPO and forms a relatively stable nitroxyl
 466 radical exhibiting very distinguishable EPR spectra. When the paints which were in contact
 467 with pure DMPO were illuminated, new lines appeared which varied with the irradiation time
 468 (Figure 6b). The separation in Gauss between the two extreme lines which appears (*) upon

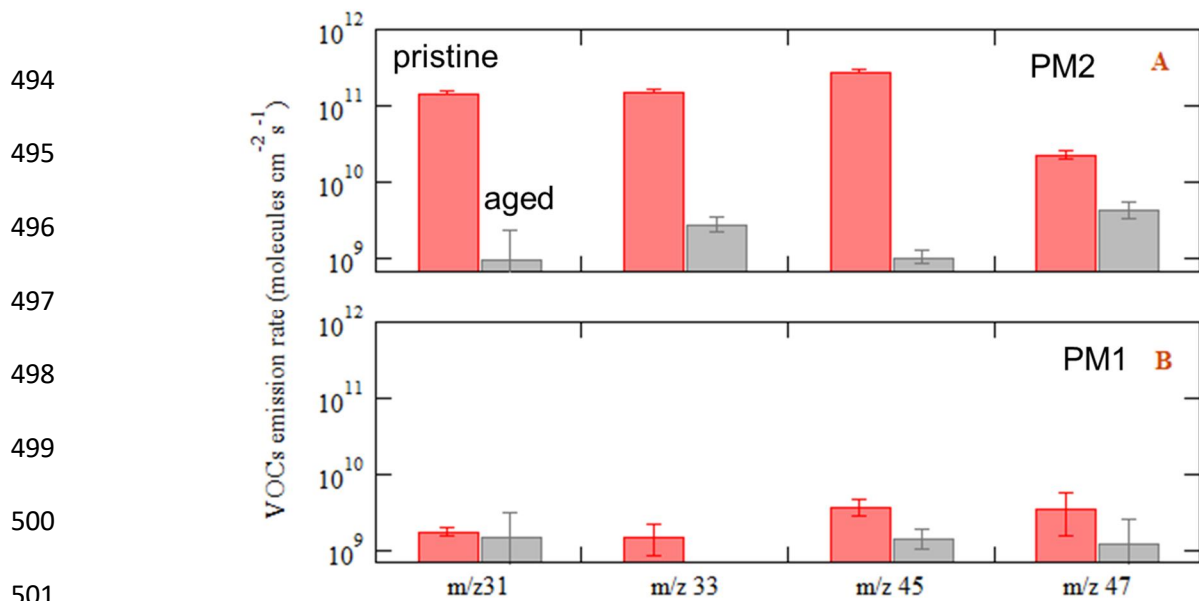
469 illumination is on the order of 42 Gauss. This fits well with hyperfine coupling expected in the
470 case of trapped $\cdot\text{OH}$ radical. Even embedded in a paint formulation, TiO_2 reacts and generates
471 $\cdot\text{OH}$ radicals at the sample surface or within the paint coat for both paints PM1 and PM2 as
472 shown in Figure 6c. The formation of $\cdot\text{OH}$ radicals upon illumination of TiO_2 and
473 polyacrylonitrile is well known mechanism and already observed^{43, 44}.

474 The photocatalytic performance of the paints was investigated, as well. In this sense, two types
475 of experiments were performed, i) on-line analysis of VOCs released by the paints upon light
476 irradiation and ii) on-line monitoring of the removal of xylene induced by the photocatalytic
477 effect of the paints. All the VOCs released from pristine and aged PM1 and PM2 paints are
478 observed on Figure 7. Four types of VOCs appeared in the reactor under illumination of the
479 paints: formaldehyde (m/z 31), methanol (m/z 33), acetaldehyde (m/z 45) and formic acid (m/z
480 47). At first glance, it can be seen that PM2 paint released a bigger amount of VOCs compared
481 to PM1, especially for non-aged samples. Thus, although these photocatalytic materials are
482 aimed to eliminate a broad range of volatile organic compounds, they release harmful
483 pollutants, such as formaldehyde, for instance. These observations are in agreement with the
484 literature data. For example, the release of formaldehyde was also observed upon light
485 irradiation of photocatalytic paints by Salthammer and Fuhrmann²¹.

486 Concerning the removal of xylene induced by the photocatalytic activity of both paints, the first
487 order rates of xylene disappearance were measured. The PM1 paint was not able to eliminate
488 xylene; hence, it was impossible to measure the corresponding rate constant. On the other hand,
489 first order rate constant of $(9.5 \pm 4.5) \times 10^{-4} \text{ s}^{-1}$ was measured for pristine PM2 and (5.7 ± 0.9)
490 $\times 10^{-2} \text{ s}^{-1}$ for the aged PM2. Hence, the aged paint containing nano- TiO_2 was much more effective
491 (ca. two orders of magnitude) in terms of photocatalytic removal efficiency towards xylene.

492

493



502 Figure 7: Surface emission rates of released VOCs for both PM1 and PM2 paints, pristine and
 503 aged ones.

504

505 DISCUSSION

506 Nano-TiO₂ is known for its photocatalytic property. Manufacturers add it in their formulation
 507 for their VOCs removal action. In this study, we reveal that the paint containing TiO₂ particles
 508 with sizes up to 100nm and rutile crystalline structure (PM1) cannot remove xylene from the
 509 air, independently of its aging state, as the decay of xylene could not be measured (see Figure
 510 2 in the supplementary information). On the other hand, the paint composed of TiO₂ NPs with
 511 anatase crystalline structure enables the degradation of xylene as the first order decay of xylene
 512 were $(9.5 \pm 4.5) \times 10^{-4} \text{ s}^{-1}$ and $(5.7 \pm 0.9) \times 10^{-2} \text{ s}^{-1}$ for non-aged and aged PM2 paints,
 513 respectively. While the photocatalytic properties of the paint improves the elimination of VOCs
 514 such as xylene, it leads also to the generation of four additional VOCs that are released in the
 515 environment at the same time. Among the four identified compounds, formaldehyde **which is**
 516 **a sensory irritant**, has been classified as carcinogenic substance⁴⁵. The benefit of the
 517 photocatalytic property to clean up the environment is counterbalanced by the emission of
 518 harmful VOCs and also by the possible release of NPs. Indeed, a high amount of NPs,

519 essentially composed of Titanium, was observed on the EDX spectrum (Figure 5b), released by
520 the aged PM2. Despite the fact that the same free radicals are generated during EPR experiments
521 of P1 and P2 powders, three lines with respective g-factors of 2.023, 2.009 and 2.004 related to
522 TiO₂ reactivity, P2 nanoparticles with anatase crystalline structure are more efficient than the
523 rutile microparticles. If the EPR peak intensities of P1 and P2 are similar when non-irradiated,
524 P2 EPR spectrum showed more intense peaks compared to P1 under UV-irradiation. P1 does
525 not act as VOCs removal agent contrary to P2 which exhibits a high reactivity under UV-
526 radiation, in agreement with the literature data^{46, 47}. A possible explanation could be that the
527 anatase crystalline structure exhibits lower recombination rates combined with higher surface
528 adsorptive capacity with organic compounds⁴⁸, leading to production of more free radicals
529 acting on VOCs. When P1 and P2 are added in a paint (so called PM1 and PM2 formulations),
530 EPR spectra show more peaks attributed to trapped •OH radicals (Figure 6 c) generated at the
531 paint surface or within the paint⁴⁴ which are responsible of the VOCs degradation. As observed
532 for irradiated P1 and P2, PM2 show more intense EPR peaks and the amount of generated •OH
533 radicals increases with the irradiated time (see Figure 6 b), confirming that nano-TiO₂ based
534 paint PM2 is indeed more reactive than PM1. Concerning the crystalline structures, it is well-
535 known that these two principal structures exhibit different photocatalytic performances⁴⁹ and
536 that a mixture of anatase and rutile showed a more pronounced catalytic effect⁵⁰, as observed
537 for PM2 containing 2.5 wt % of rutile TiO₂ microparticles and 2.5 wt % of anatase TiO₂ NPs.
538 Obviously, the increase of the produced •OH radicals at the paint surface with the irradiation
539 time corroborates the increase of the first order decay of xylene after ageing of PM2. In addition
540 to the difference in crystal structure, a carbonaceous coating was well observed by TEM (Figure
541 1b) and SAXS (Figure 2) in the case of the P1 particles which could also reduce the
542 photocatalytic property. A very thin shell of about 0.16nm was also found at the surface of the
543 P2 NPs in the dispersion D2 (Figure 2). This shell might be rather a surface contamination of

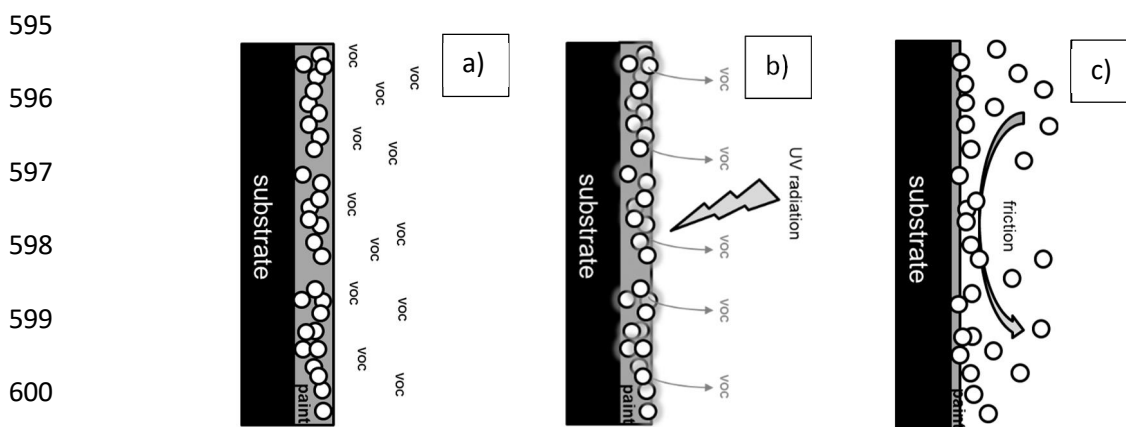
544 the NPs than a carbon coating as observed for P1 but its presence could contribute to the
545 dispersion of the NPs in an organic matrix, as for P1 particles which are intentionally coated
546 with a thin carbon layer in order to improve the compatibility between the inorganic particles
547 and the organic matrix of the paint. Indeed, if P2 NPs are agglomerated/aggregated in a solid
548 state (Figure 1d), they look really well dispersed in a liquid media, when observed by cryo-
549 TEM (Figure 1e). Furthermore, only 10% of aggregation was measured by SAXS/SANS when
550 studying D2 dispersion. As the manufacturer uses this dispersion to formulate the PM2 paint,
551 it is expected that P2 NPs would be well dispersed in the paint. However, the SEM observations
552 of PM2 following the weathering step (Figure 3d), indicate that clusters of NPs are visible but
553 also the plastic substrate, which suggests that the dispersion state of the NPs was not good as
554 expected and also that a significant degradation of the organic matrix occurred. The SEM
555 observation and XPS analysis of PM1 and PM2 performed prior and after the weathering
556 revealed a deterioration of the paint surface following the ageing of the paints. Prior to the
557 ageing, the SEM analysis showed a thin layer of organic matrix covering TiO₂ NPs on PM1
558 and PM2 (Figure 3a and Figure 3b). After climatic ageing of the paints, SEM pictures showed
559 only microparticles and NPs of TiO₂ at the surface, indicating the disappearance of the organic
560 matrix for PM1 Q-UV and PM2 Q-UV. The XPS measurements revealed a total disappearance
561 of the peaks related to the organic matrix (C-C and C-H on Figure 4d) for PM2 paint after
562 ageing compared to C1s spectra of PM1 (Figure 4a). These results highlight the total
563 degradation of the PM2 organic matrix compared to PM1. The surface degradation of the PM1
564 paint is probably only due to the UV-irradiation whereas for the PM2, the degradation can be
565 entirely ascribed to the photocatalytic effect induced by the TiO₂ NPs. At the same time, TiO₂
566 signature significantly increases as observed on Ti_{2p} and O_{2s} XPS spectra of Figure 4 e) and
567 f), in agreement with the SEM observations. A significant difference is observed for the O1s
568 spectra (Figures 4 band Figure 4e) since there is a change in the relative intensity of the C-O*,

569 O-C=O* peak related to the organic matrix and the O²⁻ peak related to TiO₂ NPs. The
570 disappearance of the organic matrix in the case of PM₂ seems to be directly linked to the
571 emission of high levels of the VOCs. The emission of four VOCs is reduced after ageing as the
572 organic matrix completely disappeared. This results also indicates that more TiO₂ NPs are
573 present at the near surface of PM₂ aged samples compared to PM₁. This accumulation of TiO₂
574 NPs at the surface allows better removal of xylene and the absence of the organic matrix leads
575 to a high amount of released TiO₂ NPs in the environment. After ageing, TiO₂ NPs can be
576 released in the environment which could affect the workers when sand old paint or when people
577 rub against a painted wall.

578 The whole process is illustrated on Scheme 1: a) Paint containing TiO₂ NPs is applied on a
579 substrate, VOCs are present in the atmosphere, b) UV irradiations activate the photocatalytic
580 effect of TiO₂ NPs; ambient VOCs are degraded as well as the organic matrix of paint leading
581 to the emission of new VOCs in the air, c) the degradation of the paint leads to TiO₂ NPs
582 accumulation at the surface of the painted walls and a slight friction causes NPs release in the
583 air.

584 **These results shows that the emitted VOCs have a direct link with the organic matrix of**
585 **the paint. The higher the content of organic composition in the matrix, the more VOCs**
586 **are created during the irradiation of the paints. In the case of non-reactive paint PM₁, a**
587 **small quantity of VOCs were emitted compared to the PM₂ one. P1 micron size particles**
588 **showed a small photocatalytic efficiency while degrading the organic matrix. As the**
589 **degradation of the matrix is weak, the same amount of emitted VOCs was observed after**
590 **aging of PM₁ paint. In contrast, the PM₂ paint, which contains anatase TiO₂ NPs, induces**
591 **greater degradation of the organic matrix due to the higher photocatalytic efficiency**
592 **which in turn leads to greater emission of VOCs prior to aging i.e. before the**

593 **disappearance of the organic matrix. After aging, a very small amount of organic matrix**
594 **was present in the PM2 paint and the concentration of emitted VOCs decreased.**



601 Scheme 1: Simplified illustration of the process leading to emission of new VOCs and release
602 of NPs in the air from the photocatalytic paints.

603

604 CONCLUSION

605 Few studies^{20,21,51} have shown that irradiation of the photocatalytic paints leads to
606 generation of VOCs in the air instead of their removal. The origin of these compounds
607 was mainly attributed to the degradation of the organic binder in agreement with our
608 findings. These few studies speculated that the cause of released carbonyl compounds
609 could be the photochemical decomposition of paint binders, without going into deeper
610 systematic investigations.

611 All these previous studies are based on off-line analytical techniques coupled to the
612 sampling methodology. Thus, the choice of the sampling support and the associated
613 analytical techniques play a crucial role during the identification of the VOCs, beyond the
614 sampling artefacts which can be issued by these methods. This indicates that the selected
615 coupling system (sampling method/analytical technique) will determine the class of
616 detected and identified VOCs. The proton transfer reaction mass spectrometry (PTR-MS)

617 offers a possibility to observe continuously and on-line a large selection of VOCs with
618 considerably reduced temporal evolution compared to the off-line techniques.

619 In this study, for the first time to the best of our knowledge, by using the state of the art
620 PTR-ToF-MS instrument we show that the tested photocatalytic paints released organic
621 compounds such as formaldehyde, methanol, acetaldehyde and formic acid upon
622 irradiation.

623 These results indicate that following only the decaying concentrations of a target
624 compound (in this study xylene) is not sufficient to make an assessment of the effectiveness
625 of photocatalytic paints towards VOCs elimination in various indoor environments. Such
626 an approach does not take into account the fact that stable reaction products, mainly the
627 harmful carbonyls, may occur which can profoundly impact the indoor air quality. These
628 VOCs emerge exclusively from the organic matrix decomposition since much lower
629 emissions were measured in the case of the aged paint which exhibits a lower amount of
630 organic composition in the matrix. In addition, the SEM pictures and XPS analysis
631 indicate that decomposition of the organic matrix induced an accumulation of TiO₂ NPs
632 at the surface of the paint followed by their release in the air. There is no direct
633 relationship between the VOCs emission and the NPs release although both phenomena
634 are caused by the photocatalytic degradation of the organic matrix.

635 Thanks to the large suite of experiments reported in this paper and the results obtained,
636 different solutions were selected to decrease the release of particles and VOCs in the air
637 and therefore to formulate a "safer-by-design" photocatalytic paint. A first approach is
638 to control the degree of the photocatalytic efficiency by modifying the TiO₂ NPs with
639 different coatings and also to control the dispersion state of the NPs in the organic matrix
640 to decrease its degradation while maintaining an optimum photocatalytic efficiency of the
641 paints. The selected coatings should have a good affinity with the organic matrix to have

642 **a good dispersion of the NPs in the paint. Another choice is localization (grafting) of TiO₂**
643 **NPs on bigger particles to prevent NPs release and to improve the affinity between NPs**
644 **and the organic matrix and to reduce the release of NPs. Finally, more resistant binders**
645 **should be tested to reinforce the organic matrix. All of the suggested solutions are**
646 **currently under investigation in our laboratory in cooperation with the manufacturer of**
647 **these paints.**

648

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654 **Notes**

655 The Authors declare no competing financial interest.

656

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