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Towards the development of safer by design mineral photocatalytic paint: influence of the TiO₂ modifications on particle release

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Environmental significance

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A safer by design product approach was employed in the development of a mineral photocatalytic paint, whereby a coating to photocatalytic TiO₂ or grafting to CNC was applied. The impact of the coating on the weathering of the paint was evaluated. Mineral matrix-based paints with TiO₂ coated by bio-inspired ligands with PEG or grafted with CNC demonstrated the lowest emission level in the aerosol fraction resulting from abrasion testing compared to the reference paint. Furthermore, no TiO₂ nanoparticles were identified in the aerosol fraction. The modification and functionalisation of TiO₂ nanoparticles enhanced the durability of the paints, regardless of the artificial weathering. Results highlight the potential for incorporating TiO₂ nanoparticles into paints for air purification, with a reduced release to the environment throughout the paint life cycle and a reduction in the potential for human exposure by inhalation.

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Towards the development of safer by design mineral photocatalytic paint: influence of the TiO₂ modifications on particle release

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The development of safe nanomaterials has become a significant concern in various industry sectors using advanced materials. While there is variability in the definitions of Safe(r) by Design (SbD), the general concept is to minimise environmental, health and safety concerns implementing appropriate measures at an early stage of product design to control exposure and hazard, thus reducing risks. The SbD product strategy applied in this paper refers to the mitigation of exposure by the identification of release scenarios during the use and the end of life of the nano-enabled products (NEPs) that include engineered nanomaterials (ENMs). This strategy was applied to the development of a photocatalytic mineral paint containing TiO₂ engineered nanomaterial. This ENM was then incorporated into a mineral matrix-based paint for photocatalytic application. The different paint formulations were applied to standardised substrates and artificially weathered in an accelerated weathering chamber with controlled parameters. Mechanical solicitation that simulate end of life (EoL) of the paint, through abrasion tests, were performed to assess the potential emission of airborne particles that could lead to human or environmental exposure. The release evaluation confirms that paints with TiO₂ nanoparticles without SbD coating release more nanometric particles due to strong matrix degradation. The TiO₂ nanoparticles coated with PEG or grafted onto CNC does not completely prevent the degradation of the paint surface during ageing. However, this degradation does not necessarily lead to an increase in aerosol emission. The coating degradation during accelerated ageing limits the degradation of the paint matrix, preventing the release of unbound TiO₂ nanoparticles. Understanding the mechanisms of release and how they are influenced by the ENMs, the matrix material and the process characteristics is crucial for the exposure and risk assessment approach in occupational settings involving engineered nanomaterials. Moreover, establishing release rates makes it possible to increase the reliability of SbD e-infrastructure for performance testing and the implementation of Safe-by-Design approaches in the nanotechnology supply chain.

Introduction

Several types of particles (e.g., cellulose, TiO₂, ZrO₂, ZnO, Ag, and CeO₂) are added to paints to impart coating performances and bring new functions to the system. The advantages of nanomodified paints include durability; chemical, erosion and abrasion resistance; decorative; dirt repellence; color; resistance to UV light; antifouling properties; and others.^{1–4} Photocatalytic paints offer a promising solution for the building industry to produce paint formulations that improve indoor air quality and therefore individual exposure to gaseous pollutants. Indeed, the oxidative photocatalytic principle offers the possibility to remove pollutants from air using only ambient sunlight and the oxygen/water molecules.^{5–8} Nevertheless,

evaluate the risk benefit ratio of developing this type of product by ensuring that this new air purification function does not create adverse effect as new sources of pollution is crucial. This is where the concept of Safe-by-Design (SbD) product comes into its own, with the integration of exposure assessment at the earliest stages of product development. This approach was included as a key design parameter into the new product development, in the same way as the expected function. The SbD concept aims to encourage the development of safer materials/products, safer production, and safer use and end-of-life by performing timely SbD assessments to reduce hazard, exposure, or both.^{9,10} The product oriented Safe by Design appears as an efficient solution but remain challenging.¹¹ Ruijter *et al* concluded that hazard screening of ENMs is complex and joint efforts between innovators, scientists, and regulators are needed to further improve SbD hazard testing. Consequently, a key element of the SbD approach to risk reduction is to mitigate exposure. The characterisation of particle emissions with a view to reducing them during the design of the new products is the primary tool for exposure reduction. This approach has already been applied in a previous study to develop a photocatalytic organic matrix-based paint containing TiO₂ nanoparticles (NPs)

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taking into consideration the safety aspects over its life cycle.^{12,13}

Titanium has been identified as a promising element for its photocatalytic properties, with potential applications in the construction sector, particularly in paints. These applications include both interior and exterior paints. The results of the studies conducted by Nieto-Márquez *et al.* indicate that around 20% of NO₂ removal efficiency recorded and validated by statistical analyses with a photocatalytic activity maintained for a year after application of the interior paint.¹⁴ Whereas the findings of Baudys *et al.* demonstrate that climatic conditions have a significant influence on the photocatalytic action, the activation of photocatalytic paint is closely linked to the roughness of the paint surface when applied outdoors.¹⁵ In addition Gandolfo *et al.* show the impact of photocatalytic paint porosity on indoor NO_x and HONO levels.¹⁶

The two key elements to be studied in the development of a SbD photocatalytic paint are the photocatalytic agent and the paint matrix. Consequently, when developing a photocatalytic paint, it is essential to study the interaction between these elements.¹⁷ This implies that the interaction and competition of the photocatalytic agent between the matrix and the external environment must be considered.¹⁸ Additionally, the interaction of the matrix with the external environment and its impact on the photocatalytic agent must be also considered.

TiO₂ is most active in the form of nanoparticles, but coating appears necessary to be developed to achieve an efficient photocatalytic effect^{6,19,20} and to avoid adverse effects on health. Indeed, TiO₂ has the potential to cause degradation of the matrix. Maqbool *et al.* shows the generation of volatile compounds from the matrix²¹, a phenomenon that was also observed by Truffier-Boutry *et al.* in a previous study. Moreover, it can also lead to the emission of aerosols from the matrix, with the potential aerosolisation of titanium dioxide nanoparticles in the form of aggregate/agglomerate.²² In order to mitigate the aforementioned adverse effect, Laisney *et al.* initiated the development of a novel generation of titanium dioxide nanoparticles (TiO₂ NPs). A polyethylene glycol coating is added during the TiO₂ NP synthesis.¹³ An initial study to develop a photocatalytic organic matrix-based paint succeeded in generating safer by design paints, thanks to the use of these specifically developed TiO₂ NPs, which exhibit similar photocatalytic properties and enhanced physical properties as compared to paints containing the commercial TiO₂ NPs. However, as not all the resistance and ageing criteria were met, it proved necessary to optimise the coating and study their incorporation into a mineral-based paint. The aim of this article is to present the main findings on aerosol emission under mechanical stress and the characterisation of the paints and aerosols involved. A new calculation of the number of particles released is proposed to facilitate the integration of these values into an e-infrastructure for exposure assessment. A separate article was devoted to the assessment of photocatalytic properties.²³

Materials and Methods

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Paints formulation

The mineral matrix-based paints were formulated by the manufacturer ALLIOS (France) from two bases, as reported in Table 1. The first mineral base is transparent (T, without TiO₂ microparticles). The second mineral base is white (W, with 10 wt% TiO₂ microparticles in rutile and minor anatase form (Fig. S1) as a white pigment. The TiO₂ microparticles have a median minimum Feret diameter of primary particles determined by SEM at 240 nm.¹² These mineral based paints were also composed of potassium silicate based matrix, vinyl acetate terpolymer organic binders, ethylene and vinyl chloride, calcium carbonate, other additives and water. The photocatalytic TiO₂ nanoparticles were incorporated into the paints to compare standard formulation paints noted T, Tn_{TiO₂}, W and Wn_{TiO₂} with safer by design paints noted W_{PEG1/1}, W_{PEG5/1}, W_{CNC13.7} and W_{CNC21.9}. Tn_{TiO₂} and Wn_{TiO₂} paints were composed of 3.5 wt% commercial anatase TiO₂ nanoparticles in the form of aggregates/agglomerates with a median minimum Feret diameter of primary particles determined by SEM at 7.2 nm.¹² The first route of new TiO₂ ENMs design is based on coating with bio-inspired ligands (route 1).¹³ For the W_{PEG1/1} and W_{PEG5/1} paints, the commercial anatase TiO₂ nanoparticles coated with PEG for the [PEG]/[Ti] ratio = 1/1 and 5/1 were added with an amount of 3.5 wt% TiO₂. The second route of design (route 2) is based on TiO₂ grafting onto CNC. For the W_{CNC13.7} and W_{CNC21.9} paints, 0.5 wt% TiO₂ nanoparticles grafted onto cellulose nanocrystals (CNC) forming CNC-TiO₂ hybrids was added in paints as slurry containing 13.7 wt% and 21.9 wt% of hybrid. These two paints were composed respectively of 0.10 and 0.16 wt% of TiO₂. Laser diffraction analysis (HORIBA, reference LA-960) is used by the manufacturer to control the dispersion of the titanium slurry in the mineral matrix paint. These eight paints were applied on LENETA (black plastic-vinyl chloride/acetate copolymer with a smooth matte surface) and standard Taber (aluminum, Taber industries, USA) substrates by a manual film applicator at a wet thickness of 150 μm and 100 μm, respectively.

Artificial weathering

These paint formulations applied on LENETA and TABER substrates underwent to artificial weathering in an accelerated weathering chamber (model QUV accelerated weathering, Q-Lab, USA) during 500 hours and 1000 hours, according to the ISO 16474-3 norm. The paints were exposed to two alternatives cycles: (i) exposure to UVB-313 lamps with irradiance of 0.71 W.m⁻² at 310 nm, a temperature at 50 ± 3 °C and relative humidity of 50% during 5 hours and (ii) exposition to water spraying at a flow rate of 7 L.min⁻¹ with temperature at 25 ± 3 °C and relative humidity of 100% during 1 hour without irradiation. This accelerated ageing scenario is designed to correspond to a paint lifetime of around 10 years in average real-life conditions.

Table 1: Compositions of the paints. * The amount of TiO₂ nanoparticles in hybrids slurry is 20wt% **. The amount of TiO₂ nanoparticles in hybrids slurry is 32wt%.

Paint formulation	Paint matrix	Formulation specificities	Amount of TiO ₂ micro (wt%)	Amount of TiO ₂ NPs (wt%)
T	Transparent mineral	Without nano and micro TiO ₂	0	0
T _{nTiO₂}	Transparent mineral	Without TiO ₂ microparticles and with commercial TiO ₂ nanoparticles	0	3.5
W	White mineral	The base paint that include TiO ₂ microparticles	10	0
W _{nTiO₂}	White mineral	Commercial TiO ₂ nanoparticles added	10	3.5
W _{PEG1/1}	White mineral	Commercial TiO ₂ nanoparticles coated with PEG ([PEG/Ti] ratio = 1/1) added	10	3.5
W _{PEG5/1}	White mineral	Commercial TiO ₂ nanoparticles coated with PEG ([PEG/Ti] ratio = 5/1) added	10	3.5
W _{CNC13.7}	White mineral	CNC-TiO ₂ hybrids added*	10	0.1
W _{CNC21.9}	White mineral	CNC-TiO ₂ hybrids added**	10	0.16

Mechanical solicitation

The mechanical solicitation was performed by abrasion on the paints applied on TABER substrate before and after artificial weathering, according to the ISO 7784-2 standard. The abrasion system and aerosol measurement was set up as shown in Fig. 1. All measurements were carried out in a 0.25 m³ glove box equipped with a HEPA filter at the bottom with a background noise lower than 5 particles per cm³. For this condition, a vacuum was done at the top of the glove box where a pump sucks the air at a flow rate of 150 L.min⁻¹.

The paint abrasions were achieved by a TABER rotary abramer (model Abraser 5135, Taber industries, USA) at a rotation speed of 60 rpm during 200 cycles. Two CS-0 type wheels set with a load of 500 g were covered by S42 abrasive sticker paper to simulate abrasion wear.

The particles released during the abrasion process were sucked by flow splitter (Flow Splitter 4-Way 3708, TSI Incorporated, USA) connected to a sampling rod at a flow rate of 13.5 L.min⁻¹. This ensured isokinetic sampling by the aerosol characterisation devices. These particles released were measured in real time by condensation particle counter (CPC, model 3775, TSI Incorporated, USA) and optical particle counter system (OPC, Fidas®Frog, PALAS, Germany) to determine the particle number concentration and particle size range (nanometric, submicronic or micro-sized). The CPC counts the aerosol particles ranging from 5 nm to 3 µm. The OPC allows to measure the aerosol particles in the range of 180 nm to 18 µm. Furthermore, the particles aerosolised were collected on a hydrophobic polycarbonate membrane (PCM, pore size 0.4 µm,

Millipore, USA) by a system filtration (3-piece carbon-filled polypropylene conductive monitor with 50 mm extension cowl, SKC®) also installed on the sampling rod. The membranes are analysed by microscopy coupled with energy dispersive X-ray spectroscopy (see the characterisation section).

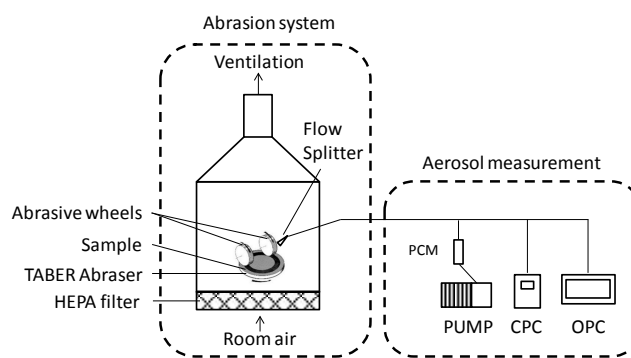


Fig. 1: Schematic representation of experimental set up for the abrasion tests. The paint abrasions were achieved by a rotary abramer. The released particles sucked by flow splitter connected to a sampling rod were measured in real time by condensation particle counter (CPC) and optical particle counter system (OPC,) to determine the particle number concentration and particle size range (nanometric, submicronic or micro-sized). Furthermore, the particles aerosolised were collected on a hydrophobic polycarbonate membrane (PCM) on the sampling rod for SEM and EDX analysis.

The design of the aerosol measurement strategy follows the current standard operating procedures for characterizing aerosol emissions at the workplace in the range of 5 nm to 8 µm, the OECD tiered approach, and the NF EN 17058:2018.^{24,25}

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Characterisation

The color of paints applied on LNETA substrate before and after artificial weathering was measured by portable spectrophotometer (color guide 45/0, BYK-Gardner, Germany) with a spot diameter of 4 mm under the standard illuminant D65 at an incidence angle of 10°. The calibration was performed with bright white and black standard plates. The colorimetric values were evaluated using the CIE 1976 L*a*b* color system. L* coordinate represents the lightness of color with values ranging from 0 (black) to 100 (white) and a* and b* were color parameters (+a* = reddish, -a* = greenish, +b* = yellowish and -b* = bluish). Three measurements at different spots were done for each paint. Total color difference (ΔE^*) was then calculated between measurements collected for the paint before artificial weathering and that after artificial weathering according to the Equation 1.

$$\Delta E_{ab}^* = \sqrt{\Delta L^*{}^2 + \Delta a^*{}^2 + \Delta b^*{}^2} \quad (1)$$

The surface morphology of paints as well as shape and size range of particles released during mechanical solicitation were investigated by Scanning Electron Microscopy (SEM-FEG, LEO 1530, Germany). All samples were coated by 10 nm thin platinum layer sputtering to avoid charging effect. The high-resolution images were acquired with a 5 kV acceleration voltage, a 3.6 mm working distance, a 30 μ m diaphragm aperture and a $\times 10k$ or $\times 100 K$ magnification. In addition, the elementary chemical composition of paints and particles released during mechanical solicitations were performed by Energy Dispersive X-ray spectroscopy (EDX, QUANTAS EDS, Bruker Nano assisted software ESPRIT, USA) in the SEM at 15 kV acceleration voltage, 8 mm working distance, 60 μ m diaphragm aperture and $\times 10 K$ magnification.

The chemical degradation of artificial weathering exposed paints were analysed by X-ray Photoelectron Spectroscopy (XPS, Versaprobe II ULVAC-PHI spectrometer, Japan) with Al K α monochromatic X-ray source of 100 μ m diameters. Survey (0-1200 eV) and high resolution (C1s, N1s, O1s, Mg2s, Al2p, Si2p, K2p, Ca2p and Ti2p) spectra were recorded using 117 and 23 eV pass energy, corresponding to 1.6 and 0.6 eV energy resolution (based on Ag 3d5/2 fwhm measurement). The binding energy of high-resolution spectra was calibrated from the carbon peak at 285 eV. The atomic percentage of elements was performed from high resolution spectra using ULVAC-PHI Multipack software.

Results and discussion

Characterisation of the paints surfaces before and after artificial weathering

In first instance, the assessment of artificial weathering is primarily based on direct visual observation and CIE colorimetric analysis. Fig. 2 shows the evolution of the paints surface deposited on LNETA substrate before and after artificial weathering carried out by a digital camera. On one

hand, CIE colorimetric analysis was investigated to evaluate the color variations of paints over UV exposure time. The results obtained for all paints before and after artificial weathering were presented in Table S1. When the artificial weathering time is 0 hour, the paint surface is uniformly white whatever the paint formulation. They also show that no changes color occurred upon aging for T, Tn_{TiO₂}, W, W_{PEG1/1}, W_{CNC13.7} and W_{CNC21.9} paints, while for Wn_{TiO₂} and W_{PEG5/1} paints, ΔE^* values increases from 0.49 to 0.80 and from 0.66 to 1.04, respectively. These increasing are mainly related to the increase b* value which involve that Wn_{TiO₂} and W_{PEG5/1} paints have yellowed with artificial weathering. However, for some paints, it was not possible to carry out a colorimetric analysis. This is because, for the standard paints, the T (without TiO₂), Tn_{TiO₂} (with commercial TiO₂ nanoparticles) and Wn_{TiO₂} (with both TiO₂) paint surfaces was degraded after 500 hours exposure while W paint surface (with TiO₂ microparticles) was unaltered after artificial weathering. The degradation of these paints can be attributed to the photocatalytic effect induced by the TiO₂ nanoparticles.²² In the case of safer by design paints, W_{CNC13.7} paint surface was degraded after 500 hours exposure while W_{PEG1/1}, W_{PEG5/1} and W_{CNC21.9} paints were degraded only after 1000 hours of UV exposure which typically corresponds to a lifetime of around 10 years in average real-life conditions. It should be noted that this scenario represents a standardised scenario (ISO 16474-3). Azimzada *et al.* have described particular environmental conditions that could lead to a greater release of the paint.²⁶ In summary, adding of TiO₂ nanoparticles coated with PEG for the [PEG]/[Ti] ratio of 1/1 and 5/1 and CNC-TiO₂ hybrid at a concentration of 0.16 wt% TiO₂ in paints (W_{CNC21.9}) enhance the stability of the paint on the substrate compare to the standard paints with pristine TiO₂ nanoparticles. The W_{PEG1/1}, W_{PEG5/1} and W_{CNC21.9} paints before and after 500 hours to exposure were optically (validated by the manufacturer with a spectrophotometer DATACOLOR, reference Spectro 700) and mechanically stable and can be considered for use on a wall.

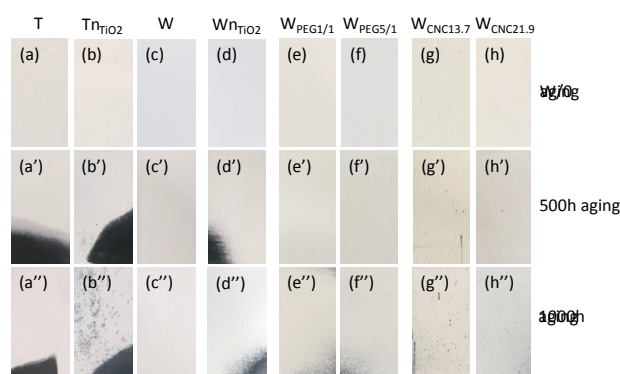


Fig. 2: Pictures of T (a), Tn_{TiO₂} (b), W (c), Wn_{TiO₂} (d), W_{PEG1/1} (e), W_{PEG5/1} (f), W_{CNC13.7} (g) and W_{CNC21.9} (h) paint deposited onto Leneta substrates before artificial weathering. The paints after 500 hours and 1000 hours exposure to artificial weathering are annotated respectively with (') and ('').

To better see the artificial weathering impact on the paints, the morphology of paint surfaces were investigated by SEM. Fig. 3 and Fig. 4 show the SEM images of T, Tn_{TiO₂}, W and Wn_{TiO₂} standard paints (Fig. 3.a, Fig. 3.b, Fig. 3.c and Fig. 3.d,

respectively) and of $W_{\text{PEG1/1}}$, $W_{\text{PEG5/1}}$, $W_{\text{CNC13.7}}$ and $W_{\text{CNC21.9}}$ safer by design paints (Fig. 4.a, Fig. 4.b, Fig. 4.c and Fig. 4.d, respectively) before and after 500 hours noted with (') and 1000 hours noted (") exposure to artificial weathering. The images are also shown with a $\times 10k$ magnification in Fig. S2. As it can be seen before artificial weathering, the particles incorporated into paints were covered by a dense layer whatever the formulation. The dense layer on W paint remains unaffected after 1000 hours UV exposure (Fig. 3.c'') while that on T paint was a bit removed after 500 hours and 1000 hours UV exposure (Fig. 3.a' and Fig. 3.a''). This observation proves that the W paint was more stable in presence of TiO_2 microparticles after artificial weathering. In the literature, the durability of paints has been improved by addition of TiO_2 pigment in the paint formulation.^{27,28} As micrometric TiO_2 (pigment) absorbs UV light, the underlying paint matrix are protected from direct degradation as well as the paint surface.²⁷ For the Tn_{TiO_2} and Wn_{TiO_2} paints, Fig. 3b' and Fig. 3.d', this layer was removed after 500 hours exposure to artificial weathering. Nevertheless, a thin layer was observed after 500 hours UV exposure on $W_{\text{PEG1/1}}$, $W_{\text{PEG5/1}}$, $W_{\text{CNC13.7}}$ and $W_{\text{CNC21.9}}$ paints surface (Fig. 4.a', Fig. 4.b', Fig. 4.c' and Fig. 4.d', respectively). However, the particles number (paint constituents) covered by this layer decrease after 1000 hours UV exposure, inducing an increase of the porosity. It was reported in the literature that the organic matrix layer at the paint surface containing TiO_2 and SiO_2 nanoparticles was degraded with artificial weathering.^{22,28} This degradation can be attributed to the photocatalytic activity induced by TiO_2 nanoparticles. This indicates that adding PEG around TiO_2 nanoparticles and grafted CNC onto TiO_2 lead to an improvement of the stability of the paint during ageing.

To get a better understanding on the observed changes of the paints after artificial weathering, the elementary chemical compositions after and before artificial weathering were analysed by EDX. Fig. S3 shows the EDX spectra of Wn_{TiO_2} , $W_{\text{PEG5/1}}$ and $W_{\text{CNC21.9}}$ paints before and after artificial weathering.

These are elements that constitute the paints. The presence of platinum on EDX spectra find its origin from the coating used for SEM analysis. However, for the Tn_{TiO_2} , $W_{\text{PEG1/1}}$ and $W_{\text{CNC13.7}}$ paints, the Cl element was attributed to one of the polymer from the organic binder disappears after 1000 hours exposure to artificial weathering. However, for the Wn_{TiO_2} paint, both K and Cl elements disappear after 1000 hours UV exposure while it remains present into T, W, $W_{\text{PEG5/1}}$ and $W_{\text{CNC21.9}}$ paints. In agreement with SEM observations, these results suggest that increasing artificial weathering time induces the degradation of mineral matrix and/or organic binder, which leads an increase of the particles number at the paint surface. Indeed, the mineral matrix is present before and after artificial weathering, excepted for the Wn_{TiO_2} paint, while the organic binder in Tn_{TiO_2} , Wn_{TiO_2} and $W_{\text{PEG1/1}}$ paints is degraded with artificial weathering. The low decrease of mineral matrix and/or organic binder for $W_{\text{PEG5/1}}$ and $W_{\text{CNC21.9}}$ safer by design paints (Fig. 4) brings them closer to the W paint (base paint with TiO_2 microparticles and without nanoparticles). At this stage these two paints are a promising in term of durability against artificial weathering.

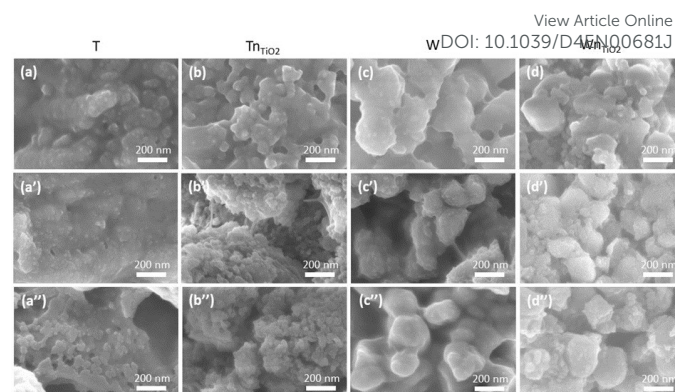


Fig. 3: SEM images of T (a), Tn_{TiO_2} (b), W (c), Wn_{TiO_2} (d) paints before artificial weathering. The paints after 500 hours and 1000 hours exposure to artificial weathering are noted respectively with (') and ("), magnification 50 K.

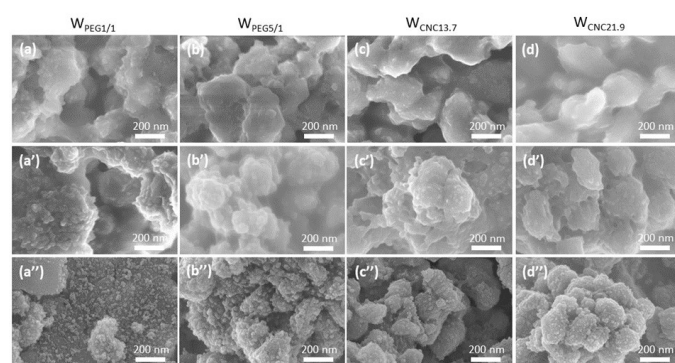


Fig. 4: SEM images of $W_{\text{PEG1/1}}$ (a), $W_{\text{PEG5/1}}$ (b), $W_{\text{CNC13.7}}$ (c) and $W_{\text{CNC21.9}}$ (d) paints before artificial weathering. The paints after 500 hours and 1000 hours exposure to artificial weathering are noted respectively with (') and ("), magnification 50 K.

The evolution of extreme surface chemical structure of artificial weathering paint were analyzed using high-resolution X Ray Photoelectron Spectroscopy (XPS) measurements (Fig. 5 and Table S2). We examine the correlation between the presence of TiO_2 particles and chemical structure degradation of the matrix. Since XPS is surface analyses technique (~ 5 nm depth analysis), prior to weathering, all samples show any Ti 2p peak signature. This represents the organic fraction of the mineral paint matrix. The C 1s core peak of Safe-by-Design PEG, is attributed to C-C/C-H and C-O bonds at 285 and 286.5 eV. The doublet centered at 293 eV is assigned to potassium compounds, characteristic of a mineral matrix. After artificial weathering, we noticed the presence of Ti 2p peak for Tn_{TiO_2} , Wn_{TiO_2} , $W_{\text{PEG1/1}}$, associated to TiO_2 ($\text{Ti}2p_{3/2}$ at 458 eV). In parallel to this process, the C 1s peak spectra emphasize a decrease of the intensity of the shoulder at 286.5 eV (C-O related bond) and the appearance of low intensity peak at 289 eV, a signature of O=C=O bonds. We notice that Ti 2p peak after weathering is in the oxidation state VI+ without any sign of titanium reduction. At the same time, the C/O atomic concentration ratio decreases (Fig. 6), indicating a change in the polymer matrix induced by the photocatalytic process driven by the presence of TiO_2 . For $W_{\text{PEG5/1}}$, this process is significantly reduced, since we observe a low titanium signature on the surface and a low change in the C 1s spectrum signature after artificial weathering. For $W_{\text{CNC13.7}}$ and $W_{\text{CNC21.9}}$ we noticed slight change in C 1s spectra after

artificial weathering with low concentration of TiO_2 at the surface (within limit of atomic concentration resolution of XPS), this might be assigned to the lowest concentration of TiO_2 in the matrix compare to PEG formulation paints.

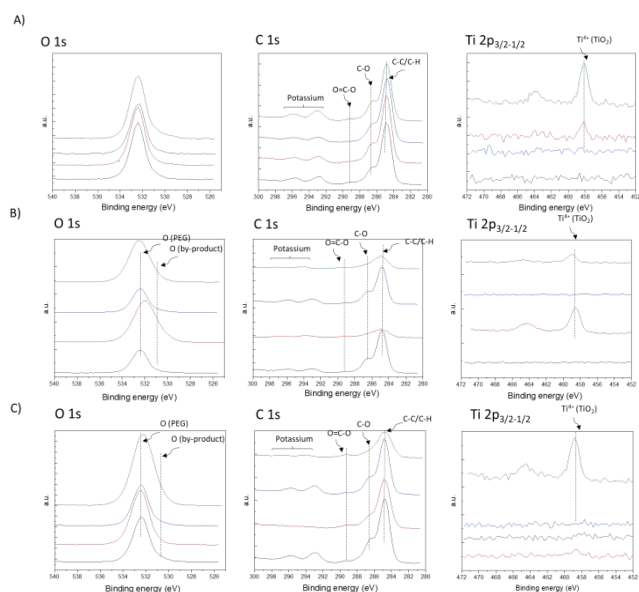


Fig. 5: C 1s, O 1s and Ti 2p XPS core level peaks recorded at the surface of (A) T (Black), TnTiO_2 (red), W (blue), WnTiO_2 (green), (B) $\text{W}_{\text{PEG}5/1}$ (black: 0 hour and red: 1000 hours), $\text{W}_{\text{PEG}13.7}$ (blue: 0 hour and green: 1000 hours) and (C) $\text{W}_{\text{CNC}13.7}$ (black: 0 hour and red: 1000 hours) and $\text{W}_{\text{CNC}21.9}$ (blue: 0 hour and green: 1000 hours) paints surface before and after artificial weathering.

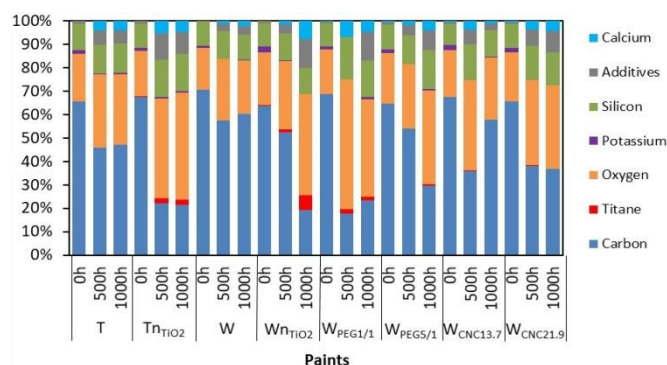


Fig. 6: Chemical compositions of the T, TnTiO_2 , W, WnTiO_2 , $\text{W}_{\text{PEG}5/1}$, $\text{W}_{\text{PEG}13.7}$ and $\text{W}_{\text{CNC}21.9}$ paints surface before and after artificial weathering.

Particles released from mechanical sollicitation

Fig. S5 illustrates the evolution of the concentration recorded for CPC and OPC over 200 cycles. The concentrations obtained for each triplicate of a sample were integrated to determine the aerosol concentration for each instrument and the results are presented in a box plot.

Particle number concentration released from standard paints (without ENMs), measured in real time by CPC and OPC during 200 seconds abrasion before and after artificial weathering, was shown in Fig. 7. It is important to note that the total concentration of particles released per cm^3 as measured by CPC was greater than that measured by OPC, except for T paint before and after 500 hours, TnTiO_2 paint after 500 hours

and WnTiO_2 paints before and after exposure to artificial weathering. This indicates that there are more nanometric particles emitted from T paint after 1000 hours, TnTiO_2 paint before and after 1000 hours and W before and after artificial weathering. For the T paint before and after 500 hours, TnTiO_2 paint after 500 hours and WnTiO_2 paints before and after exposure to artificial weathering, the total concentration of particles released per cm^3 by CPC was of the same order of magnitude as than measured by OPC. This shows that the particles aerosolised have mainly submicronic and micro-sized.

In addition, before artificial weathering, significant differences were shown between the T paint without both TiO_2 microparticles and nanoparticles and TnTiO_2 paint with TiO_2 nanoparticles and W paint with both TiO_2 . Indeed, the addition of TiO_2 nanoparticles in TnTiO_2 paint increased by a factor 16 the particle emissions in the nanometer and micrometer ranges (5 nm to 3 μm) compared to T paint. Moreover, the particles emissions are increased by factor of 306 when TiO_2 microparticles are added in W paint. Nevertheless, the presence of both micro and nano TiO_2 in WnTiO_2 paint decreased the total particle emissions compared to TnTiO_2 and W paints. This indicates that the stability of paints was improved when both micro and nano TiO_2 were added. Moreover, the aerosol particle emissions decreased when artificial weathering time increased from 500 hours to 1000 hours, except to the T and WnTiO_2 paint. For the T paint, its low surface degradation after artificial weathering, probably induced by UV irradiation leads to an increase of 2.3 times the particles concentration emission. WnTiO_2 paint after artificial weathering released 6 times more aerosol particles than WnTiO_2 paint before artificial weathering. This is related to the surface degradation of the organic binder and mineral matrix induced by TiO_2 nanoparticles during artificial weathering, as shown on SEM images (Fig. 3) and EDX and XPS spectra (Fig. S3, Fig. S4 and Fig. 5).

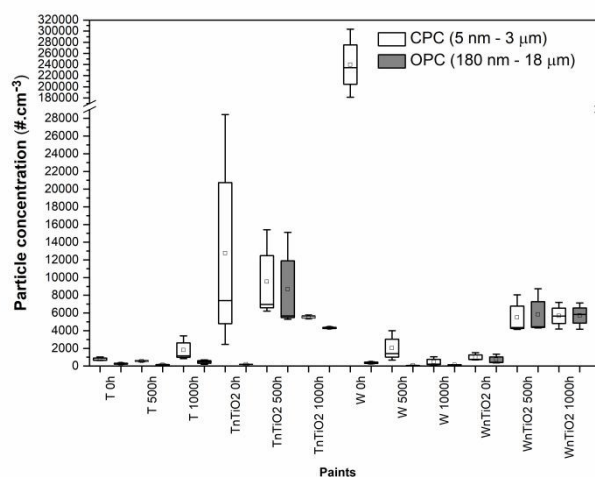


Fig. 7: Concentration of particles released per cm^3 measured by CPC in white from 5 nm to 3 μm and OPC in grey from 180 nm to 18 μm for T, TnTiO_2 , W and WnTiO_2 paints before and after 500 hours and 1000 hours exposure to artificial weathering.

The effect of the artificial weathering on the particle number concentration released from safer by design paints

monitored in real time by CPC and OPC during 200 s abrasion before and after artificial weathering was presented in Fig. 8. It shows that, whatever artificial weathering time, the concentration of particles emission from safer by design paints was below that of the reference paint W_{TiO_2} . It is important to note that the addition of TiO_2 - PEG nanocomposites and CNC - TiO_2 hybrids in paints plays a role on particles emission during the abrasion. On the other hand, before artificial weathering, total concentration of particles release measured by CPC and OPC was relatively close, excepted for the paint $W_{CNC13.7}$. This indicated that the particles released from paints have submicronic and micro-size. Moreover, paints $W_{PEG1/1}$ and $W_{CNC13.7}$ were the most emissive in particles resulting from abrasion comparison to the paint $W_{PEG5/1}$ and $W_{CNC21.9}$. Increasing the PEG concentration by a factor of 5 around TiO_2 nanoparticles in $W_{PEG5/1}$ paint resulted in a reduction in the average number of emitted particles by a factor of 7.2 compared to $W_{PEG1/1}$ paint. The same trend was observed on the emitted particles when the CNC - TiO_2 hybrids in paint $W_{CNC21.9}$ was increased compared to paint $W_{CNC13.7}$. Thus, it can be highlighted that the paint formulation, the concentration of PEG and hybrids and stability have a significant impact on the airborne released particles during the abrasion process. After artificial weathering, paints were less emissive in aerosol during the abrasion. This can be due to a loss of material resulting from artificial weathering (Table S3 and Fig. S6), which leads to a decrease of the particles emission if aerosol content in total release is unchanged compared to non-weathered paint. If not, another hypothesis is a reduction in the mechanical resistance of the paint, resulting in a reduction in the interaction energy between the Taber and the paint. This would then lead to a reduction in the emission of aerosolised particles in favour of the formation of coarse paint residues. To discriminate between these two hypotheses, further characterisation would be required to quantify aerosol and residue mass and to elucidate the morphology and effective density of the aerosol. According to previous study¹², for the paint $W_{PEG1/1}$, the number of particle released decreases by a factor 1.41 and 1.24 after 500 hours and 1000 hours UV exposure, respectively when the matrix is changed from mineral to organic, as organic matrix-based paint are degraded by photocatalytic reaction induced by TiO_2 nanoparticles. Thus, it can be highlighted that the paint formulation and stability have a significant impact on the airborne released particles during the abrasion process.

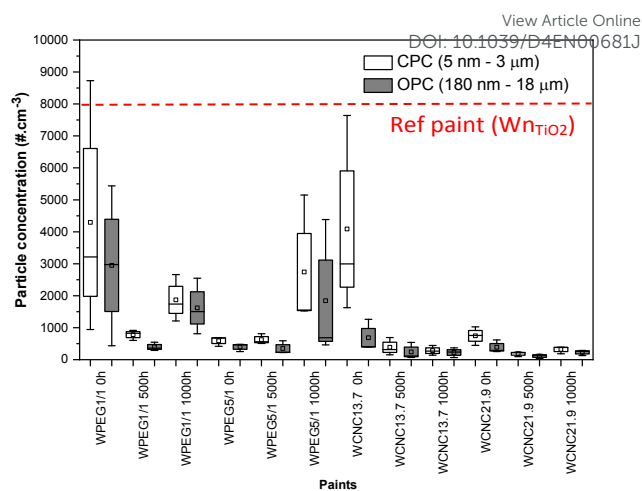


Fig. 8: Concentration of particles released per cm³ measured by CPC in white from 5 nm to 3 μm and OPC in grey from 180 nm to 18 μm for $W_{PEG1/1}$, $W_{PEG5/1}$, $W_{CNC13.7}$ and $W_{CNC21.9}$ paints before and after 500 hours and 1000 hours exposure to artificial weathering.

In order to avoid the resuspension of particles and friction between abrasive paper and Taber substrate, an evolution of the data treatment of the abrasion process has been done. To take the analysis further, the particles number concentration released measured by CPC and OPC was calculated during the first 10 s of abrasion. Here, it only takes into account that paint abrasion and does not follow the ISO 7784-2 standard, which involves an abrasion during 200 s. The particle number concentration released from reference and safer by design paints monitored in real time by CPC and OPC during 10 s abrasion before and after artificial weathering was represented in Fig. 9. As it can be seen from this graph, the population of released particles was mainly submicronic and micro-sized. Significant differences between the reference paint, W_{TiO_2} and safer by design paints were observed. Indeed, whatever artificial weathering, adding TiO_2 nanoparticles coated with PEG for the [PEG]/[Ti] ratio = 5/1 and CNC - TiO_2 hybrids at a concentration of 0.16 wt% TiO_2 in paints ($W_{CNC21.9}$) decreased the concentration of emitted particles. Moreover, for the paints $W_{PEG1/1}$ and $W_{PEG5/1}$, the increasing of PEG thickness around TiO_2 nanoparticles improves probably protection of the organic binder and mineral matrix of the TiO_2 photocatalytic action, which reduces the number of particles emitted during the abrasion. Paints containing CNC - TiO_2 hybrids with a concentration of 0.1 and 0.16 wt% TiO_2 emitted particles in number 285 #.s⁻¹ and 486 #.s⁻¹ after 1000 hours of UV exposure, respectively. The TiO_2 concentration on CNC has a direct impact on particles number released. Thus, Paints $W_{PEG5/1}$ and $W_{CNC21.9}$ are the most promising in terms of number particles emissions over time from the point of view of safer by design approach.

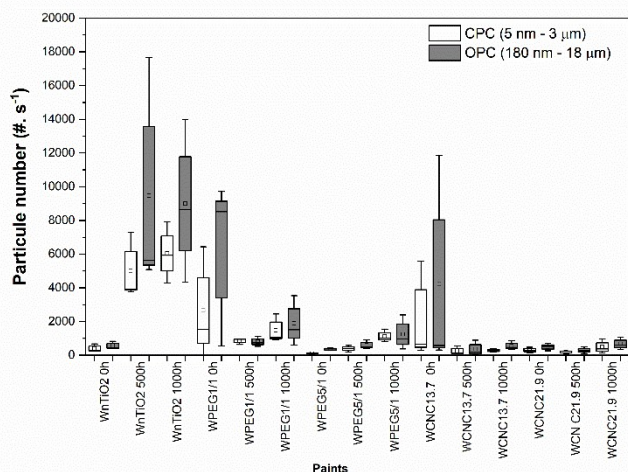


Fig. 9: Particles number released per second measured with CPC in white from 5 nm to 3 μm and OPC in grey from 180 nm to 18 μm for W_{TiO2}, W_{PEG5/1}, W_{PEG5/1}, W_{CNC13.7} and W_{CNC21.9} paints before and after 500 hours and 1000 hours exposure to artificial weathering.

The compositions of the particles released from paints in air during the abrasion were characterized by SEM-EDX to take things even further on analyses of their morphologies, size range and elementary chemical composition. Fig. 10 compares the SEM images of particles released during the abrasion from W_{TiO2}, W_{PEG5/1} and W_{CNC21.9} paints before and after artificial weathering. For the aerosol emitted before and after 500 hours artificial weathering from paints W_{TiO2}, W_{PEG5/1} and W_{CNC21.9}, SEM images show the presence of micrometric agglomerates with size ranging from 1 to 4 μm. They were mainly composed of carbon, oxygen, silicon, platinum, calcium and titanium, as investigated by EDX analysis (Fig. S7), and correspond to paint fragments. These results are in line with numerous studies showing that the fraction of the emitted particles are linked to the matrix and are not alone.^{28,29} Moreover, aluminum was also found in small quantities in the micrometric agglomerates emitted from W_{TiO2} and W_{PEG5/1} paints before and after artificial weathering. A small quantity of magnesium was also found in the micrometric agglomerates emitted from paint W_{TiO2} after 500 hours exposure to artificial weathering. In the aerosols emitted from paint W_{PEG5/1} during the abrasion, there was no alone TiO₂ nanoparticles detected, contrary to the aerosols emitted from paint W_{TiO2} after artificial weathering. In W_{TiO2}, in addition to the micrometric agglomerates, individual particles with submicronic size ranging from 200 nm to 320 nm were observed as shown in Fig. S8. Carbon, oxygen, titanium and platinum (coating for SEM analysis) were detected (Fig. S9). These individual particles are the micrometric TiO₂ pigment added to the paint formulation for its white color. Regarding aerosols emitted during the abrasion from the W_{CNC21.9} paint after 1000 hours exposure to artificial weathering, the micrometric sized agglomerates were composed of carbon, oxygen, platinum and titanium (Fig. 10 and Fig. S7), which correspond also to micrometric TiO₂ pigment added to the paint formulation. It confirms that there was no primary nanometric TiO₂ catalyst added to the paint

formulation identified in the particles released from W_{TiO2}, W_{PEG5/1} and W_{CNC21.9} paints during the abrasion. In our previous work¹², individual TiO₂ nanoparticles were released from organic matrix-based photocatalytic paints during the abrasion. Thus, interestingly, the change of matrix (i.e. organic vs. mineral) prevented the release of TiO₂ nanoparticles in air.

Consequently, to prevent and/or reduce nanoparticles releases, W_{PEG5/1} and W_{CNC21.9} paint are the most promising from a safer by design point of view.

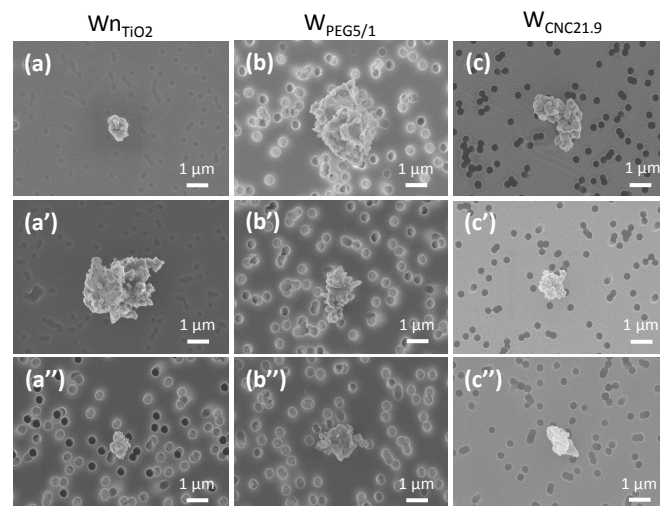


Fig. 10: SEM images of particles released from W_{TiO2} (a), W_{PEG5/1} (b) and W_{CNC21.9} (c) paints. The paints after 500 hours and 1000 hours exposure to artificial weathering are noted respectively with (') and (''), magnification 10 K.

Conclusions

A safer by design strategy has been implemented for the development of an innovative photocatalytic mineral TiO₂-based photocatalytic paint through the synthesis of new nanoTiO₂-based catalysts. This strategy includes eight formulations, comprising four standard paints with or without TiO₂ microparticles for white color and TiO₂ nanoparticles for the photocatalytic property. Four safer by design (SbD) paints have been evaluated, comprising two based on coating with PEG bio-inspired ligands (route 1) and two based on TiO₂ grafting onto CNC (route 2).

Prior to and following the application of artificial weathering, the surfaces of the paints were subjected to colorimetric analysis for paint degradation characterisation. The results indicated that TiO₂ nanoparticles incorporation conduct to a surface degradation of the standard paint after 500 hours of exposure. These observations are also confirmed by other authors.^{21,30} In addition, the TiO₂ microparticles stabilise the matrix-based paint as evidenced by SEM images showing the presence of the organic binder after 1000 hours of UV exposure on the W paint (with TiO₂ microparticles and without TiO₂ nanoparticles).

Regarding SbD paints the incorporation of TiO₂ nanoparticles coated with PEG and CNC-TiO₂ hybrid in paints, have been shown to improve the stability of the paint under artificial ageing. The smaller decrease of mineral matrix and/or

organic binder for $W_{\text{PEG5/1}}$ and $W_{\text{CNC21.9}}$ shown by SEM images and XPS analysis compare to W_{TiO_2} paint are a promising in term of durability against artificial weathering.

The evaluation of release by conducting abrasion tests on the paints confirm that standard paints emit more nanometric particles compared to SbD paints and that the released from SbD paints have submicronic and micro-size. Nevertheless, the emission rate tends to decrease with ageing. This result is counter-intuitive but can also be observed with SbD paints. Indeed, the coated TiO_2 nanoparticles do not entirely prevent the degradation of the paint's surface with aging. The new findings from this study indicate that this degradation does not necessarily result in an increase in aerosol emission under mechanical stress. The main hypothesis is that the reduction in the mechanical resistance of the paint triggers a reduction in the interaction energy between the abrasive and the paint that leads to a reduction in the emission of aerosolised particles in favour of the formation of coarse paint residues.

The concept of "safer by design" does not imply to avoid the evolution of the paint matrix; rather, it entails control of this evolution in order to achieve a balanced state. The aim is to optimise the evolution of the surface state of the paint while avoiding excessive degradation of the matrix. The SbD key parameter is to minimise the release of pollutants and particles, while enhancing the contact surface between the air and the TiO_2 nanoparticles, thereby improving the photocatalytic effect. The key role played by the evolution of the extreme surface on release rate has also been demonstrated for cement.³¹

Moreover, nature of paint matrix (organic¹² versus mineral), nanomaterials as well as artificial weathering time play important roles on shape, size and chemical composition of particles released during the abrasion. To prevent and/or reduce nanoparticles releases, adding TiO_2 nanoparticles coated with PEG for the [PEG]/[Ti] ratio of 5/1 and CNC-TiO₂ hybrid at a concentration of 0.16 wt% TiO_2 in mineral matrix-based photocatalytic paint are the most promising from a safer by design point of view.

The safe by design approach is based on a risk assessment that combines exposure and hazard. In a first approach, coating allows reducing the amount of TiO_2 , which de facto reduces risks and decrease the impact of photocatalytic properties on the paint matrix. In a previous study, the toxicity of two families of PEG- and CNC-coated titanium incorporated into an organic matrix paint was investigated.¹² This study showed no significant cytotoxic or genotoxic effects. Nevertheless, it is risky to extrapolate the toxicity of the same particles incorporated in a mineral matrix. Therefore, the exposure reduction approach presented in this paper is particularly relevant when the hazard is poorly known.

Furthermore, when the results are compared with measurements of photocatalytic properties, PEG coating appears to be the most promising for photocatalytic paint application. In fact, J. Morin *et al.* showed that TiO_2 nanoparticles coated with PEG integrated in mineral paint is a promising technical solution for indoor air decontamination with an experimental determination of the uptake coefficient of *m*-xylene in the range of $1.4 \cdot 10^{-7}$ to $3.1 \cdot 10^{-5}$.²³

Finally, a data treatment of the abrasion process has been done to avoid to take in account the resuspension of coarse particles and residues of paint. The aim is to be able to incorporate these values into exposure assessment models, which remains a major challenge for occupational safety and health regulations.³²

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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5 **Data availability**

6 The data supporting this article have been included as part of the ESI.†
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