Release Analysis of Nano-Titanium Dioxide (TiO\textsubscript{2}) from Paint: An Accelerated Weathering Experiment

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Abstract. Engineered nanomaterials (ENM’s), particularly TiO\textsubscript{2} nanoparticles are being incorporated on paints due to their capabilities to enhance optical properties and to scatter UV radiation, which eventually protects the paint from discoloration. In this study, the release of these nano-TiO\textsubscript{2} from paint was investigated. Two (2) types of paint were used, one containing pigment- and nano-TiO\textsubscript{2} (P1), while the other only contains pigment-TiO\textsubscript{2} (P2). The paints were subjected to accelerated weathering wherein the paints were exposed to cycles of UV irradiation and water condensation. The SEM-EDX results showed the distribution of the pigment- and nano-TiO\textsubscript{2} on the surface of P1 and P2, and the changes in the morphologies before and after weathering. The photomicrograph revealed the formation of cracks on the surface of P1 brought about by the photocatalytic degradation due to the presence of nano-TiO\textsubscript{2}. Leachate samples were also collected weekly in the duration of the weathering test and were analysed using ICP-OES. The presence of Ti, which can be correlated to the release TiO\textsubscript{2}, on the samples was detected. The release of Ti from P1 and P2 showed a decreasing trend throughout the weathering experiment, having the following initial amounts of release: 1.38 mg/L and 2.10 mg/L for P1 and P2, respectively. Moreover, a graphical release mechanism for the nano-TiO\textsubscript{2} release was conceptualized based on the results of the study. In general, potential release of nano-TiO\textsubscript{2} from paints could happen since these TiO\textsubscript{2} nanoparticles serve as a photocatalyst in the paint degradation when exposed to prolonged weathering conditions.

1. Introduction
Surface coatings serve as a protective layer to prevent degradation and/or hinder further deterioration of their corresponding substrates, especially when exposed to extreme environmental conditions [1]. Due to this significant role of surface coatings, several studies are being conducted to enhance their properties
and to promote desirable attributes. These include the incorporation of additives, such as engineered nanomaterials (ENM’s), on the coatings’ polymer matrices. Using ENM’s, with dimensions less than 100 nm, as additive on polymeric coatings is an area of interest in this field, since ENM’s have better properties in comparison to their bulk counterparts [2]. One important area of application of ENM’s, specifically on surface coatings, is on paints. ENM’s are usually incorporated on paints to improve properties such as chemical resistance, protection against physical deterioration like abrasion and erosion, promote surface-cleaning, anti-fouling, or anti-microbial property, and most importantly, ultraviolet light protection [2–4].

Nanoscale titanium dioxide (nano-TiO$_2$) is one of the ENM’s that has a wide range of industrial applications. It is commonly used on surface coatings, particularly on paints, as whitening agent and integrates the above-mentioned desirable properties. Furthermore, nano-TiO$_2$ on paint enhances its photodynamic properties [5]. In this regard, increased volumes of nano-TiO$_2$ are being manufactured, together with the rising demand for paints and other surface coatings. But aside from the advantages brought about by the incorporation of nano-TiO$_2$ on paints, its potential environmental risk must also be considered. Numerous researches have been conducted and predicted that relevant amounts of these nano-TiO$_2$ could end-up in the environment and the release of nano-TiO$_2$ can possibly affect living organisms to some extent [2,4]. Paints and other polymeric coatings containing nano-TiO$_2$ are often exposed to natural degradation or weathering that are initiated by different mechanical stresses and/or ultraviolet radiation from the sun. Consequently, exposure to the said conditions can result to the release of nano-TiO$_2$ from paints and other coatings to the environment, which can eventually cause environmental hazards. In the study conducted by Al-Kattan et al. (2013), it was found that after 113 cycles of weathering, only 0.007% of the total Ti (1.0 to 1.5 µg/L) released from paint with pigment- and nano-TiO$_2$ [4]. This signifies that the nano-TiO$_2$ particles were strongly embedded on the paint matrix. In addition, Zhang and his co-researchers (2017) also observed in their study the release of nano-TiO$_2$ from paints under various weathering and rainfall durations [2]. The total nano-TiO$_2$ released ranged from 0.6 to 2.3 µg/L. The release of nano-TiO$_2$ was found to be evident at low pH. Similarly, Azimzada and his co-workers (2019) studied the release of nano-TiO$_2$ from paints in cold climates [6]. Interestingly, they found that the release was greater during winter, specifically under freeze-thaw conditions. Though, only <0.001% of the total nano-TiO$_2$ were released. In relation to these release studies, the research conducted by Sun et al. (2016) showed that almost half of the yearly production of nano-TiO$_2$ (39,000 tons/year) was just being released directly into the environment [7].

Several studies have been done to investigate the quantities of nano-TiO$_2$ that are being released from various sources such as paints. Surface characterizations and morphological studies have also been employed in relation the release of nano-TiO$_2$. But majority of the studies were done by means of natural weathering which are more challenging to control and cannot be generalized due to climate differences across countries. Moreover, regardless of how the weathering experiment was conducted, the discussions on the release of nano-TiO$_2$ from the polymer matrix, such as paint, in relation to surface morphologies are still insufficient. The release mechanism of nano-TiO$_2$ is needed in detail to understand the concept of release in correlation to the factors that were considered in the study.

The main objective of this undertaking was to determine the amount of nano-TiO$_2$ released from paints through accelerated weathering conditions. The specific objectives of this study were as follows: a.) to utilize two (2) types of paint (P1-paint with pigment- and nano-TiO$_2$, and P2-paint with pigment-TiO$_2$ only); b.) to subject the painted panels with P1 and P2 under accelerated weathering conditions; c.) to characterize and compare the surface morphologies of the paints (P1 and P2) before and after weathering using scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX) and digital microscopy; d.) to quantify the amount of nano-TiO$_2$ released from the painted panels due to weathering by means of inductively coupled plasma – optical emission spectrometry (ICP-OES); e.) to determine the trend for the release of nano-TiO$_2$; and lastly, f.) propose a graphical release mechanism of nano-TiO$_2$ from paints.
Understanding the details of the release of nano-TiO$_2$ from paints is important and can be one of the key aspects to further evaluate its ecological effects. In addition, this study could contribute to the life cycle assessment of paints with nano-TiO$_2$.

This study only considered two (2) types of local paint. Elements other than titanium (Ti) or compounds other than TiO$_2$ were not quantified in the experiments performed. The study only focused on correlating the results of surface morphology characterization and the release of TiO$_2$ from the paints’ surfaces, which was further used to generate the graphical release mechanism.

2. Methodology

Two types of paint were used in this study: first was a special type of paint which contains pigment- and nano-TiO$_2$ (P1), and the other one was a regular acrylic paint which contains pigment-TiO$_2$ only (P2). Fiber cement panels (155 mm $\times$ 70 mm, $l \times w$) were prepared and painted on one side using P1 and P2 (3.80 g of paint/mm$^2$ of panel), and the other side of the panels were coated with wax. The painted panels were then subjected to accelerated weathering machine (Suga Test Instruments Co. Ltd.) for seven (7) weeks using a UV lamp with 388 nm wavelength and irradiance of 24 W/m$^2$. Exposure conditions were based on the established weathering standards for paint and related coatings and materials (ASTM D4587). In the duration of the accelerated weathering test, weekly collections of leachates were done. In this process, panels were pulled out of the weathering machine and deionized water was sprayed (with 150 mm distance) on the surface of the painted panels. The resulting leachates were then collected. Afterwards, the leachates were digested using aqua regia. Approximately 10 mL of the digested leachates for each type of paint per week were then submitted to ICP-OES (Prodigy7, Teledyne Leeman Labs) testing to determine the concentration of Ti that can be correlated to the released TiO$_2$.

Furthermore, samples of the painted panels (using P1 and P2) before and after weathering were subjected to SEM with EDX (Helios NanoLab 600i) to characterize the surface morphologies. The photomicrographs of the painted samples were also taken using a digital microscope (Keyence VHX-7000). A graph was also generated to determine the relationship of the release of Ti with the duration of the weathering experiment. Moreover, a proposed conceptual release mechanism for nano-TiO$_2$ was generated.

3. Results and Discussion

3.1. Surface morphology characterization

3.1.1. Scanning electron microscopy with energy dispersive x-ray (SEM-EDX). This characterization technique was done to investigate observable changes with regards to the surface morphologies of the painted samples. The result of SEM with EDX mapping for P1 before and after weathering were presented in Figure 1. In this study, detected Ti was correlated with the presence of TiO$_2$ on the painted surface. It can be seen from the SEM image of P1 before weathering (Figure 1.a) that TiO$_2$ nanoparticles can be observed, which was supported by the result of the EDX mapping – represented by blue dots (Figure 1.d). Initially, the weight % of TiO$_2$ is 15.7%. After P1 underwent accelerated weathering, the top polymer layer of the paint surface wore off, making the nanoparticles of TiO$_2$ exposed and more visible (Figure 1.e). Considering the EDX result after weathering, the weight % of TiO$_2$ was reduced to 13.5% after weathering, which can be observed with the slight reduction of blue dots on Figure 1.h.
Due to accelerated weathering, the exposed TiO$_2$ nanoparticles tend to be washed off from the surface of the paint which resulted to the reduction of TiO$_2$ weight %. Since the EDX mapping was done on a point basis, five (5) more points for each panel used were considered for the EDX data to be statistically significant. The average weight % TiO$_2$ nanoparticles was found to be 16.2% before weathering, whereas after weathering, the weight % if TiO$_2$ was reduced to 10.2%. As the top layer of P1 was exposed to weathering conditions, degradation of paint happened which contributed to the release of around 5% of TiO$_2$ nanoparticles.

For P2 (Figure 2), same observation with P1 was observed but in contrary, the initial concentration of TiO$_2$ on the paint is low, around 1.2 wt % (Figure 2.c). As P2 underwent accelerated weathering, the visible particles (blue dots) tend to decrease (comparison between Figure 2.d & h). This can be related to the reduction of the TiO$_2$ concentration due to weathering. Based on the EDX result, the concentration of TiO$_2$ was significantly reduced by half (0.6 wt %) after weathering. But upon considering five (5) more points on the surface of the panels coated with P2, the average weight % of TiO$_2$ was found to be 11.96% and 16.4%, before and after weathering, respectively. Instead of decreasing weight % of TiO$_2$, there was the increase in the weight %. This can be accounted to the exposure or surfacing of more pigment-TiO$_2$ on the surface of the P2 due to weathering, and instead of being released from the surface, pigment-TiO$_2$ remained intact on the surface, which cause the increase in its weight % [4].

Figure 3 presents the SEM images of P1 and P2 before and after weathering at a higher magnification (25 000 x). The SEM image for P1 before weathering clearly shows that the nano-TiO$_2$ that was observed
on the EDX analyses were strongly embedded on the polymer matrix of the paint. After weathering, it can be seen that the surface morphology of P1 changed. More spherical shaped particles were formed. This can be attributed to the degradation of paint, specifically the photodegradation of the organic binder due to the presence of nano-TiO$_2$. The particles of nano-TiO$_2$ that were incorporated on the paint matrix acts as a photocatalyst in the process of weathering; hence, resulting to the degradation of the top layer (as shown on Figure 3, after weathering of P1). The spherical shaped particles could be regarded as the chalking phenomenon, which was due to the paint degradation [8].

![Figure 3 SEM images of the surfaces of P1 and P2, before and after weathering at high magnification.](image)

Formation of spherical particles were also observed in P2 after weathering, but more intact on the polymer matrix or organic binder. Even though pigment-TiO$_2$ were present on P2, their corresponding photo-reactivity, specifically their reaction to UV light, was different from that of nano-TiO$_2$ that were present on P1 due to their differences in sizes.

3.1.2. Photomicrography. The samples painted with P1 and P2 were also observed under a digital microscope before and after weathering to observe structural or surface deterioration of the paints. After weathering for seven (7) weeks, there was an evident formation of cracks on the surface of P1 (Figure 4). Several portions of the P1’s surface exhibited crack development and potential branching of cracks. On the contrary, the surface of P2 remained the same and no significant changes were observed. The cracking of the surface of P1 was primarily due to the gradual degradation of the polymeric matrix, specifically the organic binder on the paint [2,9], in addition to the photodegradation brought about by the photocatalytic activity of nano-TiO$_2$ [8].

![Figure 4 Photomicrograph of P1 and P2 surfaces.](image)

3.2. Release of nano-TiO$_2$ from paint
The release TiO$_2$ particles were quantified in this study, particularly the nano-TiO$_2$ from P1. Collection of leachates were done weekly to determine the leached amount of Ti from the painted panels using ICP-OES. The obtained concentrations of released Ti in the duration of the weathering cycles were presented on Figure 5. After seven (7) days of weathering, 1.38 mg/L of Ti was detected on the leachate for P1. The amount of the released Ti significantly decreased thereafter, having a decreasing trend in the duration of the weathering experiment. The release stabilized after 28 days of weathering with an average release of 0.031 mg/L. Similar observations were seen with the release of Ti from P2. The initial amount of Ti release was 2.10 mg/L, but unlike P1, the release stabilized after 42 days.

![Figure 5](image)

**Figure 5** The graph of the release of Ti from P1 and P2 during the weathering cycles.

### 3.3. Graphical release mechanism

Based on the results of the surface morphology characterizations that were done, the release mechanism of nano-TiO$_2$ from P1, which was the focus of the study, was conceptualized. Figure 6 shows that due to the exposure of the paint’s surface to UV light or irradiation from the weathering chamber, and moisture or water condensed on the surface during weathering, the polymer matrix or organic binder tend to degrade (chalking phenomenon). This degradation resulted to the surfacing of more nano-TiO$_2$ that are embedded on the paint matrix, and eventually be released due to continuous weathering.

![Diagram](image)

**a.) Before Weathering**

- H$_2$O
- UV light
- pigment-TiO$_2$
- nano-TiO$_2$
- paint surface layer
- substrate
Figure 6: The conceptualized release mechanism of the nano-TiO$_2$ from paints due to accelerated weathering.

4. Conclusion

In this undertaking, the objectives of the study were satisfied. Two (2) types of paint were used, and the accelerated weathering experiment was successfully carried out using the appropriate standard. Upon the performance of the experiment, it was observed that there was the evident change in the surface morphologies of the paints used (P1 and P2), particularly for P1. Formation of spherical particles can be seen on the SEM image of P1 after weathering, which can be related to the chalking of P1. For P2, surfacing of spherical particles were also observed but somehow still embedded on the surface. This could be the reason why chalking was not visible (by naked eye) on the surface of P2, unlike P1. SEM-EDX mapping analysis further showed that weight % of Ti on selected points on the surface of P1 decreased by around 5%. On the contrary, weight % of Ti on P2 increased by 4.44%. The result of SEM-EDX analyses for P1 and P2 only showed that upon subjecting to accelerated weathering conditions, the polymer matrix or organic binder on the paints tend to degrade and wear off, exposing or showing more Ti particles bounded in the paint matrix. The increase or decrease in the weight % of Ti on the selected points only show that weathering can cause changes on the surface morphologies, which can potentially result to the release of TiO$_2$ from the paints.

Furthermore, photomicrographs showed the formation of cracks on the surface of P1, but none was seen on P2. The organic binder of P1 experienced severe degradation when subjected to accelerated weathering. Further degradation happened on P1 due to the presence of nano-TiO$_2$ which acted as photocatalyst. This resulted to the chalking of P1’s surface as seen on the SEM image. The appearance of cracks on the surface of P1 was also due to the photocatalytic degradation of the organic binder brought about by nano-TiO$_2$ photocatalyst. In this regard, cracks on the surface of P1 offers a larger surface area for the release of nano-TiO$_2$ particles which can be correlated to the detected Ti concentration on the leachates collected. In addition, although P2 only contains pigment-TiO$_2$, it still served as a photocatalyst to the degradation that happened during weathering. Although no visible chalking or cracks were observed on the surface of P2, there was still the release of TiO$_2$ particles.

References

[1] Tator K B 2018 Coating Deterioration Prot. Org. Coatings 5 462–73
[2] Zhang X, Wang M, Guo S, Zhang Z and Li H 2017 Effects of weathering and rainfall conditions on the release of SiO$_2$, Ag, and TiO$_2$ engineered nanoparticles from paints J. Nanoparticle Res. 19 5–10
[3] Lankone R S, Ruggiero E, Goodwin D G, Vilsmeier K, Mueller P, Pulbere S, Challis K, Bi Y, Westerhoff P, Ranville J, Fairbrother D H, Sung L P and Wohlleben W 2020 Evaluating performance, degradation, and release behavior of a nanoform pigmented coating after natural and accelerated weathering NanoImpact 17 1–9
[4] Al-Kattan A, Wichser A, Vonbank R, Brunner S, Ulrich A, Zuin S and Nowack B 2013 Release
of TiO$_2$ from paints containing pigment-TiO$_2$ or nano-TiO$_2$ by weathering Environ. Sci. Process. Impacts 15 2186–93

[5] Diamond S A, Kennedy A J, Melby N L, Moser R D, Poda A R, Weiss C A and Brame J A 2017 Assessment of the potential hazard of nano-scale TiO$_2$ in photocatalytic cement: application of a tiered assessment framework NanolImpact 8 11–9

[6] Azimzada A, Farner J M, Hadioui M, Liu-Kang C, Jreije I, Tufenkji N and Wilkinson K J 2020 Release of TiO$_2$ nanoparticles from painted surfaces in cold climates: Characterization using a high sensitivity single-particle ICP-MS Environ. Sci. Nano 7 139–48

[7] Sun T Y, Bornhöft N A, Hungerbühler K and Nowack B 2016 Dynamic Probabilistic Modeling of Environmental Emissions of Engineered Nanomaterials Environ. Sci. Technol. 50 4701–11

[8] van Driel B A, Wezendonk T A, van den Berg K J, Kooyman P J, Gascon J and Dik J 2017 Determination of early warning signs for photocatalytic degradation of titanium white oil paints by means of surface analysis Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 172 100–8

[9] Shandilya N, Le Bihan O, Bressot C and Morgeneyer M 2015 Emission of titanium dioxide nanoparticles from building materials to the environment by wear and weather Environ. Sci. Technol. 49 2163–70