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Behavior of TiO_2 nanoparticles during incineration of solid paint waste: A lab-scale test

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ABSTRACT

In order to assess the potential impacts posed by products containing engineered nanoparticles, it is essential to generate more data about the release of these particles from products' life cycle. Although first studies were performed to investigate the release of nanoparticles from use phase, very few data are available on the potential release from recycling or disposal of nano-enhanced products.

In this work, we investigated the behavior of TiO_2 nanoparticles from incineration of solid paint waste containing these particles. Solid paint debris with and without TiO_2 nanoparticles were treated in a lab scale incineration plant at 950 °C (combustion temperature) and in oxidizing atmosphere. The obtained ashes were also vitrified with additives and the release of Ti was finally evaluated by leaching test. From our incineration lab-scale experiment, we did not observe a release of TiO_2 nanoparticles into the atmosphere, and Ti was attached to the surface of obtained solid residues (i.e. ashes). The characterization of ashes showed that TiO_2 nanoparticles reacted during the incineration to give calcium titanate. Finally, a very low release of Ti was measured, less 1 mg/kg, during the leaching test of ashes vitrified with glass cullet and feldspathic inert. Our work suggests that TiO_2 nanoparticles added in paints may undergo to physicochemical transformation during the incineration, and that Ti found in ashes may be strongly immobilized in glass matrix. Since this conclusion is based on lab-scale experiment, further research is required to identify which nanoparticles will be emitted to the environment from a real-word-incineration system of household hazardous waste.

1. Introduction

Nowadays, an increasing amount of consumer goods contains engineered nanoparticles (ENPs). These particles have a size ranged from approximately a few nm to 100 nm (ISO, 2008) and different physical and chemical properties (e.g., lower melting points, higher specific surface areas, specific optical properties, etc.) from their bulk counterparts. Furthermore, the incorporation of ENPs into organic or inorganic matrix allow to obtain products with important added values (Arivalagan et al., 2011).

The paint industry is becoming one of the largest users of ENPs (Kaiser et al., 2013). Silver (Ag), silicon dioxide (SiO_2), zinc oxide (ZnO), or titanium dioxide (TiO_2) ENPs are added into traditional paint to improve properties as scratch/abrasion resistance (Scrinzi et al., 2011), biocidic activities (Zielecka et al., 2011), as well as photocatalytic activities in both architectural and decorative coatings (Hochmannova and Vytrasova, 2010). Among all the ENPs, TiO_2 is one of the most used with up to 10,000 t/year of worldwide production (Piccinno et al., 2012). It is mainly used for cosmetics, coating and cleaning agents, plastics, and in the cement industry (Macwan et al., 2011). The use of TiO_2 ENPs in paints can improve properties such as hardness, scrub resistance, contrast ratio gloss of paints, as well as photo-catalytic activity and UV protection (Wang et al., 2007).

Despite such undeniable advantages, ENPs are considered potentially hazardous to human health and to the environment due to properties like high surface reactivity, which is a consequence of their nanosize (Seaton et al., 2010). The possible effects of ENPs on human health and on environmental organisms have received a lot of attention and extensive research has been performed so far (Shi et al., 2013; Scown et al., 2010; Baun et al., 2008). The toxicity of TiO_2 ENPs has been widely studied both *in vitro* and *in vivo* test (Shi et al., 2013; Warheit et al., 2007; Liu et al., 2009). However, in contrast to all the effect studies, very little is actually known about the release of TiO_2 ENPs into the

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environment during the life cycle of paints and coatings containing TiO_2 ENPs (Gottschalk and Nowack, 2011). Hsu and Chein (2006) investigated the release of TiO_2 ENPs from wood and plastic coated with a suspension of TiO_2 ENPs (5 wt%) and from a tile plate coated with TiO_2 photocatalyst paint (Allstar Painintg Inc.). After different environmental stress, i.e. UV-light, wind and mechanical abrasion, it was found that UV-light and rubber knife scraping motion increased the release of TiO_2 ENP and that the particle release was highest from coated tile (Hsu and Chein, 2006). Kaegi et al. (2008) analyzed the release of ENPs from façade paints, showing that TiO_2 may be released into the aquatic environment. The TiO_2 particles detected after leaching tests were embedded in a matrix, probably the organic binder, and had size range from tens to a few hundreds nanometers in diameter. Another study focused on the release of Ag and TiO_2 ENPs from outdoor paint under laboratory and environmental conditions (Burkhardt, 2009). The study revealed that TiO_2 ENPs are rapidly washed out at the beginning of the test (8500 μg/L Ti) and decreased (<9 μg/L) after 6 months. Al-Kattan et al. (2013) investigated the release of Ti from paints containing TiO_2 pigment and TiO_2 ENPs by using a climate chamber. The results showed that paints containing TiO_2 ENPs may release only very limited amounts of materials into the environment, nearly 0.007% of the total Ti added in paint (Al-Kattan et al., 2013). Zuin et al. (2013) investigated the release of TiO_2, Ag and SiO_2 ENPs from three different paints by using standardized water immersion test for coatings. A very low release of Ti was measured (4–8 μg/l), and no TiO_2 ENPs were found in leachates (Zuin et al., 2013).

The very few previous studies are focused on application and use phase of nano-based paints, while the unintended release of ENPs from the end of life of products has been very little investigated. Walser et al. (2012) studied the persistence of CeO_2 ENPs introduced into a full-scale incinerator plant. The authors demonstrated that the majority of CeO_2 was attached on the surface of solid combustion residues without significant morphological changes. As follow, the treatment of waste containing CeO_2 ENPs is shifted to subsequent steps needed to manage solid residues as landfilling (Walser et al., 2012). Derrough et al. (2013) studied the behavior of Ag, tin (Sn) and nickel (Ni) ENPs in a laboratory scale incineration, demonstrating that a maximum air emission of 1.5×10^5 nanosized particles/cm^3 was reached during the thermal treatment. In this work the authors investigated the behavior of ENPs during thermal treatment, but they did not consider waste containing ENPs or items contaminated with ENPs that are actually managed under real-world conditions. As suggested by Nanda et al. (2003), thermal properties of ENPs are inversely proportional to their surface energy. When ENPs are embedded into another matrix their surface energy decrease and, consequently, their evaporation temperature and their melting point increase and tend to be more similar to their corresponding bulk material. Chemical reactivity is another important factor that influences ENPs' fate during thermal treatment. Roes et al. (2012) predicted the behavior of ENPs in incineration condition with a thermodynamic analysis, highlighting how TiO_2 ENPs should not incur to chemical changes in combustion temperature around 1000–1200 °C with an oxidizing atmosphere (incineration conditions). Musee (2010) highlighted the need of new waste management strategies to treat waste containing ENPs or items contaminated with ENPs (i.e. nanowaste). However, very limited information and experimental data are available concerning the fate of ENPs during waste treatment (Holder et al., 2013). According to Bystrzejewska-Piotrowska et al. (2009) and Moore (2006), the impact of nano-based products introduced to the market should be addressed before waste containing ENPs appears in the environment. It is therefore essential to carefully study the behavior of ENPs during the treatment of nanowaste.

The end of life of a paint may be very diverse (Som et al., 2011). The paint might be disposed together with the brickwork in a landfill. The coating could also be washed off (e.g. by sandblasting) when the façade is renovated. In this case the coating would end up dispersed in the environment either directly or indirectly via wastewater treatment plant. In addition a direct disposal of the façade coating (leftovers paint, discard, etc.) is possible. Then the product may be burnt in the waste incineration plant, landfilled or in the worst case enter the wastewater from rainwater that passes through the paint waste disposed of in landfill. These wastes are often considered hazardous because of the presence of toxic metals and organic solvents (US EPA, 2001). In this work we studied the behavior of TiO_2 ENPs during lab scale incineration of solid paint waste, which may be generated during the regular paint removal activities. The incineration test were performed with paint containing TiO_2 ENPs and pigment TiO_2, and with a reference paint without TiO_2, within the EU-funded NanoHouse project – Life Cycle of nanoparticles-based house coating (Grant Agreement No. 247810). The potential conversion of obtained combustion residues into glass-based material is also presented and discussed in this paper.

2. Materials and method

2.1. Sample

Paints with and without TiO_2 ENPs, named A1 and A3 respectively, were provided by industrial project partners. The composition of both paints is given in Table 1. A1 paint contains 6% of TiO_2 ENPs (as slurry; 50%) and approx. 13.6% of pigment TiO_2. A3 paint contains approx. 52% more of filler mineral calcite and 8% more of water than A1 paint. Both paints contain the same type and amount of binder, i.e. 14.6% of styrene–acrylic polymer. In addition to water, binder and filler, there are several other ingredients (e.g. biocides, thickener, defoamer, etc.) in both paints, making up about 13.6% of the total composition. We used Hombikat UV 100 TiO_2 ENPs (Sachtleben Chemie GmbH) with a declared primary crystal size <10 nm, specific surface area >250 m^2/g and melting point >1800 °C, and RC823 TiO_2 pigment (Cinkarna). Hombikat UV 100 is provided as an aqueous dispersion of 50% anatase TiO_2 ENPs and it is used to give photocatalytic properties to paint, while RC823 is a micronized rutile TiO_2 pigment (information from manufacturers). The TiO_2 ENPs were characterized by a set of analytical techniques, such as dynamic light scattering (DLS), zeta potential analysis, transmission electron microscope (TEM) coupled with Energy Dispersive X-ray (EDX) system (Smulders et al., 2012; Al-Kattan et al., 2013; Zuin et al., 2013). TEM analysis showed that TiO_2 ENPs have an average size of approx.15 nm, while the pigment

Table 1
Composition of A1 and A3 paint in grams.

Label	A1	A3
TiO_2 rutile pigment	135.8	0
NanoTiO_2 anatase slurry (50%)	60	0
Water	132.7	162.7
Soya lecithin	3.1	3.1
NaOH solution 10%	3.1	3.1
Talc filler	65.8	65.8
Grinded calcium carbonate filler	317.5	483.3
Styrene–acrylic copolymer dispersion (50% solids)	146.2	146.2
Silicone defoamer	109.7	109.7
Potassium siliconate	10.4	10.4
Coalescing agent	8.4	8.4
Biocide Acticide MBS (MIT/BIT)	3.1	3.1
Polyurethane thickener (solids content 25%)	4.2	4.2
Sum	1000	1000