Science of the Total Environment 476–477 (2014) 298–307

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Formulation effects on the release of silica dioxide nanoparticles from paint debris to water

Stefano Zuin [a,*], Andrea Massari [a], Arlen Ferrari [b], Luana Golanski [c]

[a] *Venice Research Consortium, Via della Libertà 12, c/o VEGA park, 30175 Venice, Italy*
[b] *GFC Chimica Srl, Via Marconi 73, 44100 Ferrara, Italy*
[c] *CEA Commissariat à l'Energie Atomique et aux Energies Alternatives, rue des martyrs 17, 38000 Grenoble, France*

HIGHLIGHTS

- The influence of paint formulation on release of Si from paint debris was studied.
- The release of Si was 1.8% with respect to initially amount of Si in paint.
- Agglomerates SiO_2 nanoparticles were found in some leachates.
- The pigment volume concentration (PVC) influences release of SiO_2 nanoparticles.
- By adjusting the properties of the binder it is possible to reduce Si release.

ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form 7 January 2014
Accepted 7 January 2014
Available online 25 January 2014

Keywords:
Engineered nanoparticles
Paints
Leaching test
Pigment volume concentration
Binder

ABSTRACT

Waterborne paints with integrated nanoparticles have been recently introduced into the market as nanoparticles offer improved or novel functionalities to paints. However, the release of nanoparticles during the life cycle of nano-enhanced paint has only been studied to a very limited extent. The paint composition could determine in what quantities and forms the nanoparticles are released. In this work, paint formulations containing the same amount of silicon dioxide (SiO_2) nanoparticles but differing in the pigment volume concentration (PVC) and in amount and type of binder and pigment, were studied through leaching test to investigate the influence of these parameters on release of Si from paint. The results indicate greater release of Si, about 1.7 wt.% of the SiO_2 nanoparticles in the paint, for paint formulated with higher PVC value (63%), suggesting that the PVC is a crucial factor for release of SiO_2 nanoparticles from paints. This hypothesis was also based on the fact that agglomerates of SiO_2 nanoparticles were only found in leachates from paint with higher PVC. A paint sample with the higher amount of binder and less calcite filler exhibited a lower release of Si among the paints with a low PVC value (35%), and no SiO_2 particles were detected in leachates collected from this paint. This could be due to the fact that a high portion of binder forms a suitable matrix to hold the SiO_2 ENPs in paint. The paint sample in which the amount of calcite was partially substituted with TiO_2 pigment did not show an important reduction on Si release. Our work suggests that paint debris containing SiO_2 nanoparticles may release a limited amount of Si into the environment, and that by adjusting the properties of the binder in combination with common pigments it is possible to reduce the release of SiO_2 nanoparticles.

1. Introduction

The exploitation of engineered nanomaterials (ENMs) by the paint industry has the ability to improve the performance of paints (Kaiser et al., 2013). Examples of such applications containing ENMs, that have been commercialized, include silica (SiO_2) engineered nanoparticles (ENPs) for improving the scratch/abrasion resistance of transparent paints (Scrinzi et al., 2011), silver (Ag) ENPs due to their biocidic activities in paint (Zielecka et al., 2011), as well as titanium dioxide (TiO_2) and zinc oxide (ZnO) ENPs which can be used as photocatalytic oxides in architectural and decorative paints (Hochmannova and Vytrasova, 2010; Saber et al., 2012).

The potential risks of ENMs have recently received a lot of attention due to toxicologically relevant properties of these materials (i.e. size, shape, surface features, etc.). Completed and ongoing research in the EU and the US is assessing the potential risks posed by ENMs for human health and the environment. The assessment of risk needs to take into account the widespread use of products containing ENMs, and cannot exclude a potential exposure to ENMs during the whole lifecycle of such products (Reijnders, 2009; Som et al., 2010). To date, there are few available studies about the release of ENMs from nano-

---

[*] Corresponding author. Tel.: +39 041 5093019; fax: +39 041 5093074.
E-mail address: sz.cvr@vegapark.ve.it (S. Zuin).

0048-9697/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2014.01.029

based consumer products (Gottschalk and Nowack, 2011), and these studies are especially focussed on nano-based textile products (Benn and Westerhoff, 2008; Kulthong et al., 2010; Lorenz et al., 2012; Windler et al., 2012) and plastics (Vilar et al., 2013; Göhler et al., 2013; Ogura et al., 2013). With regard to ENPs containing paint, the recent experiments of Kaegi et al. (2008, 2010), showed that TiO_2 and Ag ENPs may be released from exterior facades paints into surface waters. Through detailed microscopic investigations and bulk chemical analysis of runoff sample, the authors demonstrated a leaching of Ag and TiO_2 ENPs during rainfall conditions. The release of TiO_2 ENPs has been demonstrated for commercial Pilkington Activ™ paints following an accelerated aging of this photocatalytic paint under water flow and UV exposure (Olabarrieta et al., 2012). Al-Kattan et al. (2013) investigated the release of Ti from paints containing pigment TiO_2 and TiO_2 ENPs by using a climate chamber to simulate environmental weathering and a leaching test to study the influence of various parameter as UV-light, water composition and type of support. 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). We have recently investigated the release of Ti, Ag and Si from paints containing TiO_2, Ag and SiO_2 ENPs, respectively (Zuin et al., 2014). Panels coated with these paints were exposed to UV light and abraded to simulate weathering. The three paints were also leached in lab scale tests in static conditions to study the release of Ti, Ag and Si. We observed a very low release of Ti (approx. 8 μg/l) after prolonged water immersion (120 h), while the Ag measured in leachates was under detection limit (0.1 μg/l). A small release of Si was measured in leachates, with 73 mg/l of Si released from paint containing SiO_2 ENPs. After 156 h in contact with water, the total loss of Si from un-weathered and weathered panels was 245 mg/m^2 and 365 mg/m^2, respectively. Microscopic results highlighted that SiO_2 ENPs were mainly released in form of agglomerates with other particles, and only very few single SiO_2 ENPs were found in leachates. The results confirmed that Si migration is related to immersion cycles (wetting and drying cycles) of tested paints.

The characterization of ENMs released is a crucial component for the assessment of the environmental risk posed by these new substances, especially when ENMs undergo transformation reactions in the environment following release (Nowack et al., 2012; Al-Kattan et al., 2013). Therefore the ENMs released into the environment may be completely different from the materials originally added in products, and may pose new risks for human health and the environment (Som et al., 2011). According to Nowack et al. (2012), the ENMs materials released during use and disposal of nano-enhanced products may be categorized as “product-modified ENMs”, “product-weathered ENMs” and “environmentally-transformed ENMs”.

However the release of ENPs from spent paint debris is largely unknown. Such debris and fragments may be generated during the regular paint removal activities as paint scraping, dry stripping and abrasive blasting (US EPA, 2011, 2007). As commercial and industrial paints sold today may contain toxic chemicals such as biocides, it is very important that the removal, management and disposal of paint residues containing toxic chemicals is done properly to prevent any adverse effects on human health and the environment (US EPA, 2011). Vaajasaari et al. (2004) demonstrated that harmful compounds remain in solid paint debris and may be leached into the environment when paint residues are in contact with water at landfill sites. Also, the direct environmental impacts of spent residues containing antifouling chemicals generated during the regular maintenance of boats have received increasing attention in recent years (Jessop and Turner, 2011; Singh and Turner, 2009; Holmes and Turner, 2009; Turner et al., 2009). Fragments of colored paint generated during sanding or blasting of boat hulls may release toxic biocide as zinc (Zn) and copper (Cu), and have the potential to be transported over greater distances and be exposed to a wider range of environmental conditions (Jessop and Turner, 2011; Turner, 2010).

Generally, all paints contain the same constituents a polymeric binder, pigments, solvent, and additives (Bierwagen and Huovinen, 2010). The binder (resin) gives the thin layer of paint film its continuity and adhesion to the material being painted. The binder also binds pigments and fillers together and influences durability, flexibility etc. Binders include synthetic or natural resins, i.e. acrylic, polyurethanes, melamine resins, etc. Pigments are the dry materials added to the paint to give it color, and resistance properties, etc. Pigments can be divided into primary pigments and filler pigments (Tracton, 2006). Primary pigments are usually granular solids/micron-sized powders that give the paint its color and opacity. Typical filler pigments like calcium carbonate, mica, silica, and talc, are often used as extenders due to their low cost. The solvent may be organic or water (i.e. water based paint). Solvents are added to paints to disperse or dissolve the binder and to modify the viscosity of the paint. In addition to these common components there are several other additives, as coalescents, thickeners, dispersants, defoamers, biocide, etc. (Tiarks et al., 2003). ENPs are generally added in paints as slurry or powders (Keles, 2009). A characteristic parameter of paint is the pigment volume content (PVC) (Tiarks et al., 2003). The PVC represents the volumetric ratio between pigment and solid binder, given as a percentage (Gaylarde et al., 2011). This important parameter determines not only gloss and permeability, but also thermal and mechanical properties of paint (Rodrıguez et al., 2004; Vesely et al., 2012). In addition to PVC, the pigment distribution is another critical parameter determining paint properties (Bierwagen and Huovinen, 2010). For example, the high PVC in flat paint is obtained by using a combination of relative high portion of cheap filler material such as $CaCO_3$ and small amounts of TiO_2, which is needed to achieve sufficient hiding power (Tiarks et al., 2003). However, to obtain maximum hiding power with a minimum amount of expensive TiO_2, a homogeneous distribution of the pigments is essential otherwise the only result is the increasing of surface roughness with the reduction of gloss (Tiarks et al., 2003).

This work presents and discusses the effect of PVC, TiO_2 pigment content and polymer binder on the release of SiO_2 ENPs from paint. The work was performed on paint debris by using a standardized leaching test. Among various ENPs that have found commercial application SiO_2 ENPs are widely used as additives in paint, cosmetics, drugs, printer toners, and food (Scrinzi et al., 2011). Experimental paints with SiO_2 ENPs were formulated for the scope, and a paint sample without SiO_2 ENPs was used as reference.

2. Materials and methods

2.1. Paint formulation

The following composition (wt.%) of water-based paints was formulated by the industrial project partners for the scope (Table 1).

Table 1
Compositions (in wt.%) of paint tested.

Label	C1	C1a	C1b	C1c	C2
SiO_2 ENPs suspension (35 wt.%)	13.5	13.5	13.5	13.5	–
Calcium carbonate	46	25	13	28.3	46
TiO_2 pigment	–	–	15	–	–
Binder 1	23.3	44.3	41.3	–	23.3
Binder 2	–	–	–	41	–
Water	12.2	12.2	12.2	15.2	25.7
Texanol	3	3	3	–	3
Dispersant	0.8	0.8	0.8	0.8	0.8
Thickener	0.5	0.5	0.5	0.5	0.5
Defoamer	0.3	0.3	0.3	0.3	0.3
Hexa-metaphosphate	0.2	0.2	0.2	0.2	0.2
Preservative	0.2	0.2	0.2	0.2	0.2
PVC	63	35	35	35	60
SC (weight)	64	53	55	59	59
SC (volume)	45	40	40	47	41

Note: PVC = pigment volume concentration; SC = solid content; Binder 1 = styrene acrylic copolymer dispersion; Binder 2 = acrylic copolymer dispersion.