Characterization of abrasion-induced nanoparticle release from paints into liquids and air

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Abstract. Two standard methods for the characterization of the abrasion nanoparticle release into air and liquid from coatings containing nanoparticles were developed. Details of the abrasion processes and the measurement methods are shown. Paints were formulated in an industrial facility. Standard abrasion conditions in wet environments were simulated. The size distribution of the particles abraded into liquid was analyzed by a laser granulometer: submicrometric and micrometric particles were observed, but no nanometric particles. The nanoparticles released in liquid were deposited on filters for SEM (Scanning Electron Microscopy) analysis. No free or agglomerated nanoparticles were observed by SEM: nanoparticles seem to remain embedded in the paint matrix. The same coatings were abraded in the air using another standard method. The ELPI (Electrical Low Pressure Impactor) was used to determine the number size distribution of the dust generated. Abrasion is found to produce submicrometric and micrometric particles in the air but no nanoparticles. Further characterizations by SEM confirmed that no free or agglomerated nanoparticles were emitted: nanoparticles seem to remain embedded in the paint matrix.

1. Introduction

The Nanoparticles (NP) defined as objects with three external dimensions in the nanoscale range (approximately 1 nm to 100 nm) cf. standard ISO/TS 27687, find every day new industrial applications. Nanoparticles embedded in paint coatings give them very interesting properties: eg highly resistant to bacteria, better protection against UV. But this new industry can really take off only if it takes part of a responsible development for humans and the environment. Today in the absence of reliable data on the toxicity of nanoparticles, the only way to guarantee a risk close to zero is to verify that paints containing NP do not release their NP. This implies in particular the control of the implementation of nanoparticles in consumer products throughout their life cycle: during their manufacture, use and until the end of life of these nano-products. No standard methods for the characterization of abrasion-induced nanoparticle release are currently available. Standard methods for investigation of wear resistance to abrasion in dry and wet environments are used by the paint manufacturers. However, these methods have to be adapted today for paints containing NP, in order to measure if this NP could be released by the abrasion process or not.

The Taber Abrader is used in standards methods in order to abrade a large variety of products: paint coating, metal, paper, floor coating and textiles. One method for the characterization of the abrasion induced nanoparticles release into air from surface coatings was developed using a circular
Taber abrader [1]. In this case, the total number of generated nanoparticles and submicron particles was extremely low [1]. Another method was developed using a linear Taber Abrader for the characterization of nanoparticles release from polymers coatings, fabrics and nano-products like socks [2-4]. The abrasion process was optimized to give the highest release of nanodust using standards tools [4]. To our knowledge no method for the characterization of the abrasion nanoparticle release into liquid from coatings containing nanoparticles was developed.

The objective of this work is to simulate the wear of the paints induced by domestic use and to characterize the nanoparticle abrasion-induced release into liquid and air. For this purpose two measurement methods were developed: one using an Elcometer abrader coupled to off-line colloid measurements. Second, using a circular Taber abrader coupled to appropriate aerosol measurement techniques. Results of dust release under wet and dry abrasion from paints containing TiO$_2$ nanoparticles are shown.

2. Materials and methods

2.1. Description of the paints

Paints containing TiO$_2$ nanoparticles and TiO$_2$ pigment of pigmentary TiO$_2$ were formulated and applied in an industrial facility following the conditions described by the standard NF EN ISO 11998. The biocide (Mergal 723K), dispersant (Orotan 731) and against foam Byk 024 were dispersed in water. The pulverizers were introduced by increasing order of oil intakes: nanoTiO$_2$, TiO$_2$ pigment of pigmentary TiO$_2$ and calcium carbonate. Four types of paint were prepared: a nanoTiO$_2$ paint containing calcium carbonate and nanoTiO$_2$, TiO$_2$ paint containing calcium carbonate and TiO$_2$ pigment of pigmentary TiO$_2$, paint without TiO$_2$ containing only calcium carbonate and nanoTiO$_2$ and TiO$_2$ paint containing nanoTiO$_2$ and TiO$_2$ pigment of pigmentary TiO$_2$.

A Natrosol 250 HBR gel was added in order to control the mixture viscosity. At the end, a styrene-acrylic binding agent and a coalescent were added. The paints used to perform wet abrasion tests were applied on a PVC substrate. Drying of these films was performed during 20 days. The thickness of the films was estimated around 150µm. The same paints were formulated and applied on a glass substrate in order to induce dry abrasion. Drying of these films was performed during 15 days.

2.2. Measurement method for the characterization of abrasion-induced nanoparticles from paints into liquid

2.2.1. Abrasion process. For wet abrasion an Elcometer 1720 abrader was used. The abrader takes a liquid solution from a pump and spreads it out on the coating. The abrasive buffer is linearly rubbed on the sample in order to generate a dynamic friction. The abrasion conditions applied cf. standard NF EN ISO 11998 are summarized in Table 1.

| Buffer       | Abrasive action | Utilisation | Liquid solution                      | Speed       | Cycles |
|--------------|-----------------|-------------|--------------------------------------|-------------|--------|
| Abrasive buffer | Soft            | Paints      | 2.5 g/L of dodecylbenzenesulfonate of sodium | 37 cycles/minute | 200    |

This standard describes the resistance of a paint to abrasion and leaching through time. Usually, the abrasion resistance is determined by the mass loss obtained by weighing the sample before and after the abrasion process. In this work other aspects were investigated: the solutions emitted were collected and analyzed.

2.2.2. Measurement method. One instrument was used for measuring the number size distribution of the abraded particles in the liquid solution: a laser granulometer. It uses a laser beam passing through a
sample of particles in suspension in liquids and collects light intensity at different angles. Mie light scattering theory calculations and standard mathematical methods for solving the inverse problem are applied to the intensity data to generate a distribution of particle sizes that is consistent with the observed light intensities at the observed angles. The Mastersizer allows the determination of particle number distribution in the range of 0.01 µm to 1000 µm. These granulometers give no information about the type of nanoparticle measured. To address this issue the liquid was deposited on a substrate for SEM analysis. In this way the nanoparticles released were analyzed in order to determine their type: NP in agglomerate or free form or moreover NP embedded in the paint matrix.

2.3. Measurement method for the characterization of abrasion-induced nanoparticles from paints into air

2.3.1. Abrasion process. For abrasion of surface paints in the air the Taber Abrader (type 5131, Taber Industries, USA) was used. This test reproduces the aging effect induced by a mechanical friction. As indicated on Table 2, three different tools were used simulating different mechanical actions intensities. S42 tool simulates sanding process of a surface and CS10, CS17 tools simulate abrasion process. The abrasion conditions conform standard NF EN ISO 7784-1 and NF EN ISO 7784-2 are summarized in Table 2. The composition of the wheels is shown as well (see Table 2).

| Type  | Composition                                | Abrasive action | Weight | Number of cycles | Type        |
|-------|--------------------------------------------|-----------------|--------|------------------|-------------|
| Wheel CS10 | Rubber and aluminium oxide particles  | Soft             | 1 kg  | 1000             | Wheel CS10  |
| Wheel CS17 | Rubber and aluminium oxide particles  | Medium ++        | 1 kg  | 1000             | Wheel CS17  |
| Wheel S42 | Abrasive sticker paper: 12.7mmx165mm, 180ANSI-CAMI | Hard +++        | 500 g | 200              | Wheel S42   |

2.3.2. Measurement method. All manipulations are performed in a sealed glove box equipped with a HEPA filter in order to limit the initial presence of particles in the atmosphere. The background noise in the sealed glove box is quantified to less than 20 part./cm³. These special conditions are obtained by creating a vacuum at the top of the box, that will suck the air rich in particles at a rate of 150 L/min and a clean air is obtained using an absolute filter placed in the bottom of the glove box. Nanomaterials are mechanically solicited by abrasion using a standardized circular Taber equipment. Two wheels are rubbed on the sample in order to generate a dynamic friction. The friction is circular and cyclical on the surface of the sample. The particles released are sucked by a sampling line at a rate of 10.6 L/min into the ELPI. This instrument is used for measuring the number size distribution in the range of 7 nm to 10 µm. This device is capable of achieving real-time measurements and displays, for each size class, changes in concentration over time. It also allows capturing released particles on filters. These filters (hydrophilic polycarbonate membrane) are then analyzed by SEM to observe the morphology and size of the collected particles. Thus, it is possible to measure the size distribution and to perform physical-chemical characterization of the collected particles. These characterizations were performed in order to determine if nanoparticles are released by abrasion or sanding in free or agglomerated form or embedded in paint matrix.

3. Results

3.1. Size distribution of wear paint particles into liquid
The size distribution of wear particles measured by laser granulometer for nanoTiO₂ and TiO₂ paint, for nanoTiO₂ and for the paint without TiO₂ is showed on Figure 1. The x axis show the size, while the
y axis shows the relative intensity of the scattered light converted, using Mie theory, to a volume distribution.

![Graph showing size distribution of wear particles for nanoTiO$_2$, nanoTiO$_2$ and TiO$_2$ paint and the paint without TiO$_2$ given by the laser Granulometer.](image)

**Figure 1.** Size distribution of wear particles for nanoTiO$_2$ paint, nanoTiO$_2$ and TiO$_2$ paint and the paint without TiO$_2$ given by the laser Granulometer.

Particle size distribution between 0.3 µm and 700 µm are observed for the three paints. Submicrometric and micrometric particles were released. No nanoparticles released from the paints are observed whatever the composition.

3.2. Characterization of particles released into liquids

SEM analysis by retrodiffusion were performed on paint with nanoTiO$_2$ and TiO$_2$ (see Figures 2, 3a and 3b).

![SEM image of the paint with TiO$_2$ and nanoTiO$_2$.](image)

**Figure 2.** SEM image of the paint with TiO$_2$ and nanoTiO$_2$.

![SEM image of a TiO$_2$ nanoparticle embedded in a polymer matrix.](image)

**Figure 3.** SEM image of a TiO$_2$ nanoparticle embedded in a polymer matrix a) with a zoom X 10 and b) with a zoom X 50.
Bright TiO$_2$ particles with size around 200-300 nm and nanoTiO$_2$ particles with size around few nm were observed (Figures 2, 3a, 3b). The sizes of these particles correspond to the indications given by the supplier. Ti atoms have an atomic mass higher than carbon (contained in the polymer matrix) and thus emit more retrodiffused electrons. Therefore, TiO$_2$ particles and nanoparticles appear brighter on the SEM images. As represented on Figures 3a and 3b nanoparticles are embedded in the polymer matrix therefore no free or agglomerated nanotitanium particles were observed. Bigger particles with size around 20 µm could be observed as well which corresponds to CaCO$_3$ particles size given by the supplier. These particles are embedded in the polymer matrix as well (see Figure 2). SEM characterizations confirm that under wet abrasion, submicrometric and micrometric particles were released, but no free nanotitanium particles.

3.3. Paints dust emissions
The size distributions of wear particles for paint with nanoTiO$_2$ by comparison with the size distribution of the background of the glove box, given by the ELPI are showed on Figures 4 and 5.

![Figure 4](image1.png) **Figure 4.** Size distribution of the background of the glove box.

![Figure 5](image2.png) **Figure 5.** Size distribution from paint with nanoTiO$_2$ abraded using S42 wheels during 200 cycles.

The background noise is quantified less than 20 part./cm$^3$ (Figure 4). Low particles release was detected in the submicronic range (~ 0.3 µm) increasing from 10 particles/cm$^3$ to 120 particles/cm$^3$ during the abrasion process (Figure 5). No nanoparticles were emitted. This result cannot be explained by a low quality of the aspiration system.

Indeed when the glass substrate was abraded important release of particles coming from the substrate was measured (Figure 6).

![Figure 6](image3.png) **Figure 6.** Size distribution from the substrate abraded using S42 wheels during 200 cycles.
Significant release: 40 000 part/cm$^3$ was measured on channel 2 which attests the high quality of the aspiration system.

Dust emissions from nanoTiO$_2$ and TiO$_2$ paint and the paint without TiO$_2$ in the air using different tools were measured using the ELPI granulometer. The total concentration released and the sizes obtained are summarized in Table 3.

**Table 3.** Dust emissions from nanoTiO$_2$ and TiO$_2$ paint and the paint without TiO$_2$ in the air using different tools

|                  | Tools => | CS10                                      | S42                                      |
|------------------|----------|-------------------------------------------|------------------------------------------|
| **Paint without TiO$_2$** |          |                                           |                                          |
| Nanometric       | -        |                                           | -                                       |
| Submicronic      | -        |                                           | 1,021$\mu m < D_p < 1,655 \mu m$       |
|                  |          |                                           | $2,52 \mu m < D_p < 10 \mu m$           |
|                  |          |                                           | Comparable to the background            |
| Micronic         | -        |                                           | Comparable to the background            |
| **Paint with TiO$_2$+nanoTiO$_2$** |          | 0,26$\mu m < D_p < 0,381 \mu m$ C= 55 particules/cm$^3$ | 0,109$\mu m < D_p < 0,173 \mu m$ C= 170 particules/cm$^3$ |
| Submicronic      | 0,611$\mu m < \varnothing < 0,946 \mu m$ C$\leq 25$ particules/cm$^3$ |                                           |                                          |
| Micronic         | 3,99$\mu m < D_p < 10 \mu m$ Comparable to the background | 1$\mu m < D_p < 10 \mu m$ Comparable to the background |

Under dry abrasion, submicrometric and micrometric particles were released. No nanometric particles were emitted. Very low release of particles was detected: maximum 170 particles/cm$^3$ were measured using tool S42 around 150 nm and not in the nanometric range. Negligible concentrations of particles were emitted using CS17 tool therefore results are not shown in the Table 3. In conclusion, very few particles were released whatever the paint and whatever the tool.

3.4. Characterization of particles released into the air

Paints abraded using S42 wheels were observed by SEM (see Figures 7a and 7b). These wear particles were collected on the second filter stage 3 of the ELPI.

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**Figure 7a.** SEM observation of detected abraded particles on ELPI filter.  

**Figure 7b.** Zoom on abraded particles.
No free or agglomerated TiO$_2$ nanoparticles were observed: TiO$_2$ nanoparticles (~ 30 nm) seem to remain embedded in the paint matrix (see on fig.7b) which is a zoom image on abraded nanoparticles. Agglomerates of matrix particles having sizes around 110 nm are observed. The sizes vary between 100 nm and 300 nm.

4. Conclusions

Two methods for characterizing abrasion-induced nanoparticle release from paints into liquids and air were developed.

Under wet abrasion, submicrometric and micrometric particles were released, but no nanometric particles.

Tested paints present high quality in terms of degradability: under dry abrasion using different tools very low release of micronic and submicronic particles was detected while no nanometric particles were detected.

SEM images showed no free nor agglomerated nanoparticles released during abrasion in the air and liquid: nanoparticles seem to remain embedded in the paint matrix.

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