Experimental protocol to investigate particle aerosolization of a product under abrasion and under environmental weathering

Neeraj Shandilya, Olivier Le Bihan, Christophe Bressot, Martin Morgeneyer

TITLE:

Experimental protocol to investigate particle aerosolization of a product under abrasion and under environmental weathering in view of ensuring its nanosafety-by-design

AUTHORS
Shandilya, Neeraj
Direction des Risques Chroniques
Institut National de l'Environnement Industriel et des Risques (INERIS)
Verneuil en Halatte, France

Génie des Procédés Industriels
Université de Technologie de Compiègne (UTC)
Compiègne, France
neeraj.shandilya@utc.fr

Le Bihan, Olivier
Direction des Risques Chroniques
Institut National de l'Environnement Industriel et des Risques (INERIS)
Verneuil en Halatte, France
olivier.le-bihan@ineris.fr

Bressot, Christophe
Direction de risques chroniques
Institut National de l'Environnement Industriel et des Risques (INERIS)
Verneuil en Halatte, France
christophe.bressot@ineris.fr

Morgeneyer, Martin
Génie des Procédés Industriels
Université de Technologie de Compiègne (UTC)
Compiègne, France
martin.morgeneyer@utc.fr

CORRESPONDING AUTHOR
Morgeneyer, Martin
Génie des Procédés Industriels
Université de Technologie de Compiègne (UTC)
Compiègne, France
martin.morgeneyer@utc.fr

KEY WORDS
Nanomaterials, Particles; Nanosafety-by-design, Product design, Abrasion, Weathering, Emission, Aerosol

SHORT ABSTRACT
In this article, results on the emission of engineered nanomaterials, in the form of aerosols are presented, once they are subjected to mechanical solicitation and environmental weathering. These results have been obtained using a specific experimental set-up which is described in details.

LONG ABSTRACT
The present article advocates the approach of nanosafety-by-design of nanostructured products for their durable development. This approach is basically a preemptive one in which the focus is put on minimizing the emission of engineered nanomaterials' aerosols during the usage phase of the product's life cycle. This can be attained by altering its material properties during its design phase without compromising with any of its added benefits. In this article, an experimental methodology is presented to investigate the nanosafety-by-design of three commercial nanostructured products through their mechanical solicitation and environmental weathering. The mean chosen for applying the mechanical solicitation is an abrasion process and for the environmental weathering, it is an accelerated UV exposure in the presence of humidity and heat. The eventual emission of engineered nanomaterials is studied in terms of their number concentration, size distribution, morphology and chemical composition. For the given test samples and experimental conditions, it was found that the application of the mechanical stresses alone emits the engineered nanomaterials' aerosols in which the engineered nanomaterial is always embedded inside the product matrix, thus, a representative product element. In such a case, the emitted aerosols comprise of both nanoparticles as well as microparticles. But if the mechanical stresses are coupled with the environmental weathering, then the eventual deterioration of the product, after a certain weathering duration, may lead to the emission of the free engineered nanomaterial aerosols too.

INTRODUCTION
With a rapid maturity in the nanotechnology, its advancement is driven by rapid commercialization of products containing *Engineered Nanomaterials* (ENM) with remarkable properties. As described by Potocnick[1] in the article 18(5) of Regulation 1169/2011, issued by the European Commission, ENM can be defined as "any intentionally manufactured material, containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm to 100 nm". Moreover, the products containing ENM, either in their solid bulk or on their solid surfaces or in their liquid suspensions, can be termed as *Nanostructured products*. Different types of ENM with different formulations and functionalizations are used in such products according to the nature of application and budget. The products can be in the form of coatings, paints, tiles, house bricks, concrete etc.

As far as the research is concerned, one may also find enormous number of publications on the innovations that have been accomplished through nanotechnology. Despite this enormous research, the appealing traits of ENM are under probe for potential health or environmental dangers due to their tendency to get released or emitted in air in the form of aerosols during the use or processing of the nanostructures products (for example Oberdorster *et al.*[2], Le Bihan *et al.*[3] and Houdy *et al.*[4]). Kulkarni *et al.*[5] defines an aerosol as the suspension of solid or liquid particles in the gaseous medium. Hsu and Chein[6] have demonstrated that during the use or processing of a nanostructured product, a nanostructured product is subjected to various mechanical stresses and *environmental weathering* which facilitate such an emission.

According to Maynard[7], upon exposure, these aerosols of ENM may interact with human organism through inhalation or dermal contacts and get deposited inside the body which consequently may cause various detrimental effects, including the carcinogenic ones. Thus, a thorough understanding of the ENM emission phenomenon is of paramount importance given

101 the unprecedented use of nanostructured products, as mentioned by Shatkin *et al.*[8]. This may
102 not only help in avoiding unanticipated health related complications arising from their
103 *exposure* but also in encouraging public confidence in nanotechnologies.
104
105 Nevertheless, the exposure related problem has now started getting attention by the research
106 community and has been recently highlighted by various research units throughout the world
107 (for example, Hsu and Chein[6], Göhler *et al.*[9], Allen *et al.*[10], Allen *et al.*[11], Al-Kattan et al.[12],
108 Kaegi et al.[13], Hirth *et al.*[14], Shandilya *et al.*[15, 31, 33], Wohlleben *et al.*[16], Bouillard *et al.*[17],
109 Ounoughene *et al.*[18]). Considering the large scale deployment of nanostructured products in
110 the commercial markets, the most effective approach to tackle the problem would be a
111 preemptive one. In such an approach, a product is designed in such a way that it is "nanosafe-
112 by-design" or "Design for safer Nanotechnology" (Morose[19]) i.e. low emissive. In other
113 words, it maximizes their benefits in problem solving during its use while emitting a
114 minimum amount of aerosols in the environment.
115
116 To test the nanosafety-by-design during the usage phase of a nanostructured product, the
117 authors present an appropriate experimental methodology to do so in the present article. This
118 methodology consists of two types of solicitations: (i) *mechanical* and (ii) *environmental*
119 which aim at simulating the real life stresses to which the nanostructured product, a masonry
120 brick, is subjected to during its usage phase.
121
122 (i) A linear abrasion apparatus which simulates the mechanical solicitation. Its original and
123 commercial form, as shown in figure 1 (a), is referenced in numerous internationally
124 recognized test standards like ASTM D4060[20], ASTM D6037[21] and ASTM D1044[22].
125 According to Golanski *et al.*[23], due to its robust and user-friendly design, its original form is
126 already being used widely in industries for analyzing the performance of products like paint,
127 coating, metal, paper, textile, etc. The stress being applied through this apparatus corresponds
128 to the typical one applied in a domestic setting, for example, walking with shoes and
129 displacement of different objects in a household (Vorbau *et al.*[24] and Hassan *et al.*[25]). In
130 figure 1 (a), a horizontally displacing bar moves the standard abradant in a to and fro motion
131 over the sample surface. The abrasion wear occurs at the contact surface due to the friction at
132 the contact. The magnitude of the abrasion wear can be varied by varying the normal load
133 (F_N) which acts at the top of the abradant. By changing the type of the abradant and normal
134 load value, one may vary the abrasiveness and hence the mechanical stress. Morgeneyer *et*
135 *al.*[26] have pointed out that the stress tensor to be measured during abrasion is composed of
136 normal and tangential components. The normal stress is the direct result of the normal load,
137 i.e. of F_N whereas the tangential stress is the result of the tangentially acting friction process,
138 measured as force (F_T) and it acts parallel or anti-parallel to the direction in which abrasion
139 takes place. In the original form of this abrasion apparatus, one cannot determine F_T.
140 Therefore, the role of the mechanical stresses during the aerosolization of ENM cannot
141 completely be determined. To eradicate this limitation, as described in details by Morgeneyer
142 *et al.*[26], we have (a) modified it by replacing the already installed horizontal steel bar by a
143 replica in aluminum 2024 alloy and (b) mounted a strain gauge on the top surface of this
144 replicated aluminum alloy bar. This is shown in figure 1 (b). This strain gauge has 1.5 mm of
145 active measuring grid length and 5.7 mm of measuring grid carrier length. It is made of a
146 constantan foil having 3.8 μm of thickness and 1.95 ± 1.5% of gauge factor. A proper
147 measurement of the mechanical stresses are ensured through a dynamic strain gauge amplifier
148 which is connected in series to the strain gauge, thus allowing a reliable measurement of the
149 strain produced in the gauge. The data transmitted via amplifier is acquired using a data
150 acquisition software.

151
152   *[Place figures 1 (a) (b) here]*

153
154   In the figure 2, the complete experimental set-up is shown where this modified Taber
155   abrasion apparatus is placed under the conformity of a nanosecured work post. A particle free
156   air is constantly circulating inside this work post at a flow rate of 31000 l/min. It has a
157   particle filter efficiency of 99.99% and has already been successfully employed by
158   Morgeneyer *et al.*[27] in various nanoparticles' dustiness tests.

159
160   *[Place figure 2 here]*

161
162   The motor of the abrasion apparatus is kept outside and its linearly sliding part is kept inside
163   a self-designed *emission test chamber*, with dimensions, 0.5 m × 0.3 m × 0.6 m, (details in Le
164   Bihan *et al.*[28]). It helps in preventing the abrasion apparatus' motor emissions from
165   interfering in the test results. The sampling of the generated aerosol particles is done inside
166   the proximity of a radial symmetric hood (volume of 713 cm^3). By employing such a hood,
167   the aerosol particles losses due to their deposition on the surfaces can be minimized. The
168   other advantage includes increase in the aerosol particles number concentration due to a
169   relatively lower volume of the hood with respect to the emission test chamber. Thanks to this
170   set up, a real time characterization and analysis of the particle aerosols getting generated
171   during the abrasion wear can be done experimentally in terms of their *number concentrations*,
172   *size distributions*, *elemental compositions* and *shapes*. According to Kulkarni *et al.*[5], the
173   number concentration of ENM aerosols can be defined as "the number of ENM present in
174   unit cubic centimeter of air". Similarly, the size distribution of ENM aerosols is "the
175   relationship expressing the quantity of an ENM property (usually number and mass
176   concentrations) associated with particles in a given size range".

177
178   A ~~Condensation P~~particle Counter (~~CPC;~~ measurable size range: 4 nm to 3 μm) measures the
179   aerosol particles number concentration (**PNC**). ~~An~~ **The** ~~Aerodynamic P~~particle **s**~~S~~izer**s** (~~APS;~~
180   measurable size range: **15 nm**~~0.5~~–20 μm) ~~and Scanning Mobility Particle Sizer (SMPS;~~
181   ~~measurable size range: 15–600 nm)~~ measure the particle size distribution (**PSD**). An aerosol
182   particles sampler (described in details by R'mili *et al.*[30]) is used for the particle collection
183   through filtration technique on a porous copper mesh grid which can be used later in
184   Transmission Electron Microscope (TEM) for various qualitative analyses of the released
185   particles.
186   (ii) The environmental solicitation can be simulated through accelerated artificial weathering
187   in a weathering chamber, shown in figure 3. As shown by Shandilya *et al.*[31], the weathering
188   conditions can be kept in conformity with the international standards or be customized
189   depending upon the type of simulation. The UV exposure is provided via xenon arc lamp
190   (300−400 nm) installed with an optical radiation filter. The action of rain is simulated by
191   spraying deionized and purified water onto them. A reservoir is placed beneath the test
192   samples to collect the runoff water. The collected water or leachate can be used later to
193   perform the ENM leaching analysis.

194
195   *[Place figure 3 here]*

196
197   **PROTOCOL**

198
199   NOTE: The technique presented in the Protocol here is not only limited to the presented test
200   samples but can be used for other samples as well.

201
1. Artificial weathering [CEREGE platform, Aix en Provence]

1.1) Take a 250 ml sample of the deionized and purified water to be sprayed in a beaker. Immerse the tip of the water conductivity meter into the water. Note the water conductivity. Repeat the process and note the water conductivity each time.

NOTE: According to the *ISO 16474*[32], it should never be higher than 5 μS/cm.

1.2) After measuring the conductivity, connect the water source to the reservoir **of the weathering chamber** present underneath the stainless steel hood (shown in figure 3)~~.~~.

1.3) **Connect the overflow spout on the back of the chamber to a drain opening through a hose pipe.**

1.4) Place the nanocoating samples to weather ~~(details are provided later in the *Results* section)~~ ~~inside~~ **into** the stainless steel hood and close the door. **To enable a statistical evaluation of the results, use a minimum of three identical nanocoating and reference samples.**

1.5) On the digital console**, present on the front of the weathering chamber**, select a two hours cycle composed of 120 min of UV light, 102 min dry and 18 min water spray.

1.6) **Enter the number of cycles equal to 2658 which corresponds to 7 months.**

1.7) **Choose the irradiance level of the xenon arc lamp equal to 60 ± 5 W/m^2.**

1.8) **Set the ambient temperature at 38 °C.**

1.9) **Start the weathering test by pressing the LAUNCH button on the console.**

2. Abrasion and ENM aerosols characterization [INERIS S-NANO Platform, Verneuil]

NOTE: Before using**,** ~~the particle aerosol characterizing instruments i.e. CPC, APS and SMPS, they are~~ pre-~~verified~~ **verify the particle aerosol characterizing instruments** on a calibration bench of INERIS S-NANO Platform which comprises of separate and already installed reference counter parts. By following a specific protocol, ~~the~~ **ensure that the** instruments are ~~ensured to be~~ working properly.

2.1) Assemble all the units and instruments shown in the experimental set-up and make the necessary connections as shown in figure 2 (details on the units and setting up of instruments are provided in Shandilya *et al.*[33])

2.2) Switch on the circulation of the particle free air inside the nanosecured workpost by pressing the FLUX ON button.

2.3) Make this particle free air to pass through the emission test chamber by opening the chamber and keeping it open inside the nanosecured work post.

2.4) **To set up the experiment**~~In the present experimental set-up~~, **connect** the ~~CPC~~**particle counter** ~~is~~ directly ~~connected~~ to the emission test chamber to measure the instantaneous number concentration of the particles inside the chamber. A digital console on the ~~CPC~~

counter shows the concentration value directly. While the particle free air is passing through the chamber, continue to monitor this instantaneous number concentration value until it drops to zero. In this way, **ensure that** the chamber ~~can be assured to be~~**is** free of any background particle.

2.5) In the meantime, chamfer the edges of the standard cylindrically shaped abradant ~~(6 mm diameter with 2 cm length; SiC abrasive particles with an average size of 6 μm embedded in clay matrix)~~ **by gently turning its one end in a to and fro motion inside the slot** ~~using~~ **of** a tool provided with the abrasion apparatus.

2.6) **Using a digital balance with a measurement precision of at least 0.001 g,** ~~W~~**w**eigh the abradant and sample to be abraded ~~(three commercial nanostructured products in the present case) with a with a measurement precision of at least 0.001 g~~.

2.7) Once done, fix the chamfered abradant to the vertical shaft of the abrasion apparatus through a chuck present at its bottom.

2.8) Place the nanostructured product to be abraded gently beneath the fixed abradant and ~~make the necessary arrangements to~~ firmly fix its position **on the mounting system**.

2.9) Open the aerosol sampler and, by using a tweezer, place a copper mesh grid inside the slot with its brighter side upwards. Put a circular ring over the grid to fix it.

2.10) Close the sampler and connect it to a pump via a filter on one end (i.e. towards darker side of the grid) and to the particle source on the other end (i.e. towards brighter side of the grid). Mount the required normal load on the vertical shaft using the dead weights.

2.11) Through ~~CPC~~**the particle counter**, check if the background particles concentration inside the open chamber has dropped to zero. If not, wait for it. If yes, close the door of the emission test chamber.

2.12) Via the digital consoles on the instruments, manually set the flow rates of ~~CPC~~ **the particle counter** ~~equal to 1.5 l/min with 1 s of sampling time, SMPS~~**and the sizers** ~~equal to 0.3 l/min with 120 s of sampling time and APS equal to 5 l/min with 5 s of sampling time~~.

2.13) Set the total sampling duration at 20 min for all these three instruments. Set the abrasion duration and speed equal to 10 min and 60 cycles per minute respectively in the abrasion apparatus.

2.14) Connect the strain gauge to the dynamic strain gauge amplifier. Connect the dynamic strain gauge amplifier to the computer which shall be used for the data acquisition using software installed in it.

2.15) Open the software.

2.16) Click NEW DAQ PROJECT to open a new data acquisition file.

2.17) Stop the option for live data acquisition by clicking LIVE UPDATE

301   2.18) Click 0 EXECUTE to set the reference signal value equal to zero.

302

303   2.19) Switch back on the live data acquisition by clicking LIVE UPDATE.

304

305   2.20) Click VISUALIZATION to choose the mode of data representation.

306

307   2.21) Click NEW to open the templates.

308

309   2.22) The option SCOPE PANEL can be chosen, for example.

310

311   2.23) Start the data acquisition in ~~CPC, APS and SMPS~~**the particle counters and sizers** at
312   once.

313

314   2.24) After a delay of approx. 5 min, start the abrasion.

315

316   2.25) Click START in the data acquisition software window to acquire the strain gauge
317   signals corresponding to the ongoing abrasion.

318

319   2.26) After 2 min, switch on the pump connected to the MPS.

320

321   2.27) Keep the pump running for 2-4 min depending upon the quantity of the emission of the
322   aerosol particles.

323

324   2.28) Once the abrasion stops, switch off the data acquisition by clicking STOP.

325

326   2.29) Save the acquired data by clicking SAVE DATA NOW

327

328   2.30) After the **counter and sizers** ~~CPC, APS and SMPS~~ stop acquiring data, open the
329   emission test chamber and weigh again the abradant and abraded nanostructured
330   product.

331

332   2.31) Continue the entire process for every abrasion test.

333

334   2.32) Once the abrasion tests are done, the three particle aerosol characterizing instruments
335   are once again verified on the calibration bench of INERIS S-NANO Platform.

336

337   **3. TEM analysis of the liquid suspensions- Drop deposition technique [INERIS**
338   **calibration Platform, Verneuil]**
339   3.1) Prepare a 1% volume diluted aqueous solution of the liquid suspension by adding 1 part
340   of the suspension in 99 parts of the filtered and de-ionized water.

341

342   3.2) Open the cover of the glow discharge machine

343

344   3.3) Set the following operating conditions: 0.1 mbar, 45 mA, 3 min duration.

345

346   3.4) In order to make a TEM copper mesh grid hydrophilic by its plasma treatment, put it on
347   the metal stand. Close the cover and start the motor. After 3 min, it stops automatically.

348

3.5) Take out the hydrophilic turned mesh grid using a tweezer. Place it gently with its brighter side up. Deposit a drop of the diluted solution (8 μl approx.) onto the hydrophilic mesh grid using a syringe.

3.6) Allow the mesh grid to dry in a closed chamber so that the water content gets evaporated and the constituent particles rest deposited on the grid. Make sure that the mesh grid doesn't get charged with the stray particles.

3.7) **Once ready, put the grid in the TEM probe and carry out the microscopic analysis.**

3.8) **If the grid appears too laden with particles to analyze, lower the dilution percentage and volume of the deposited drop.** ~~Modify the volume of the deposited drop depending on the particles number observed by TEM microscopy.~~ The maximum volume an operator is able to deposit is approximately equal to 12 μl.

REPRESENTATIVE RESULTS
Test Samples
The protocols presented in the article were applied to three different commercial nanostructured products. A focus is put here on the details of the experimental approach:
(a) alumino-silicate brick reinforced with TiO_2 nanoparticles, (11 cm x 5 cm x 2 cm). It finds its frequent application in constructing façades, house walls, wall tiles, pavements etc. Its material properties along with a scanning electron microscope image are shown in table 1 and figure 4 respectively.

[Place figure 4 here]
[Place table 1 here]

(b) ~~Photocal Masonry and Tipe E502, P~~photocatalytic nanocoatings ~~. The two~~ consist**ing** of anatase titanium dioxide nanoparticles with a PMMA **and alcoholic base** as dispersant**s respectively**~~in the former while an alcoholic base as dispersant in the latter~~. The Transmission Electron Microscope (TEM) analysis of the two nanocoatings, shown in figures 5 (a) and (b), reveal average TiO_2 particle size equal to 8 ± 4 nm in the former case while 25 ± 17 nm in the latter. Also, two distinct phases contributed by the dispersant (in grey color) and incorporated TiO_2 nanoparticles (in pitch black color) can also be observed. The volume percentages of titanium dioxide nanoparticles in the two nanocoatings are same and equal to 1.1%. The Energy dispersive X-ray analysis (EDX) of the elemental composition of the two nanocoatings, obtained after following the protocol for the drop deposition technique, show similar observations i.e. C (60 to 65% in mass), O (15 to 20% in mass) and Ti (10 to 15% in mass). It should be noted that both nanocoatings are manufactured specifically for applications on external surfaces of the buildings which are generally porous like brick, concrete, etc. Therefore, the substrate chosen for the nanocoating application was a commercial plain masonry brick (11 cm $\times$ 5 cm $\times$ 5 cm).

[Place figures 5 (a) and (b) here]

(c) ~~NANOBYK-3810, a t~~Transparent glaze additive **consisting of nanoparticles of CeO_2 having a primary size of 10 nm. It is dispersed in the glaze with 1.3% volume percentage. Such glaze** ~~which~~ is generally applied on externally lying painted wooden surfaces to impart protection towards their eventual discoloration and weathering with time. ~~It consists of nanoparticles of CeO₂ having a primary size of 10 nm and dispersed in the glaze~~

399 ~~with 1.3% volume percentage.~~ In figures 6 (a) and (b), TEM image and elemental
400 composition analysis of a sample drop are shown respectively.

402 *[Place figures 6 (a) and (b) here]*

404 **Emission from the nanostructured brick**
405 The evolution of the total worn mass of the nanostructured brick (M_t) during abrasion is
406 shown with respect to F_N in figure 7. For each value of F_N, the abrasion test has been
407 repeated thrice. This evolution appears to follow a linear path up to $F_N = 10.5$ N after which
408 it unexpectedly increases for the higher loads. The standard deviations, measured in the
409 values of the worn mass, range from 0 to 0.023 g. The worn mass of the abradant during each
410 abrasion test was less than 2% that of the brick, therefore negligible.

412 *[Place figure 7 here]*

414 In figure 8, the unimodal PSD of the emitted aerosol particles ~~(as measured by SMPS and~~
415 ~~APS)~~ are shown for different values of F_N. For each value, the abrasion test has been
416 repeated thrice. With an increasing F_N, the mode of the PSD is also increasing. However,
417 beyond 10.5 N, the number concentration peak or the maximum particle number
418 concentration remains stagnant at ~645 cm^{-3}.

420 *[Place figure 8 here]*

422 In figure 9 (a), the evolution of the total PNC is shown with respect to F_N. For the particles
423 having sizes in the range of 20–500 nm ~~(measured using SMPS)~~, it appears to increase up to
424 10.5 N after which it starts decreasing. For 0.5–20 µm size range ~~(measured using APS)~~, it
425 increases continuously. However, it seems to approach a constant value beyond 10.5 N.
426 However, the behavior of total PNC with respect to the increasing F_T, shown in figure 9 (b) is
427 different as it increases monotonously. A similar observation can be observed for the PSD
428 modes too.

430 *[Place figures 9 (a) (b) here]*

432 For the TEM analysis of the sampled aerosol particles which were collected on a mesh grid
433 during the abrasion at 4 different values of F_N, the sizes of 50 different aerosol particles were
434 measured for each grid, and their average sizes were determined in each case. Table 2 shows
435 the average values. A clear increase in the average size of the sampled aerosol particles can
436 be seen with the increasing F_N.

438 *[Place table 2 here]*

440 **Emission from the photocatalytic nanocoatings**
441 To test the emission of aerosol particles from the photocatalytic nanocoatings, abrasion tests
442 of their weathered and non-weathered test samples were done. The results pertaining to their
443 non-weathered samples are presented first. The PNC curves obtained when the 4 layered
444 nanocoatings' test samples were abraded under a normal load of 6 N are shown in the figures
445 10 (a). The test was repeated thrice under same conditions. For uncoated reference, the
446 repetition was done on the same brick. In the figure 10 (a), the abrasion starts at t= 240 s and
447 ends at t= 840 s. Before and after this time interval (t= 0 to 240 s), the system is idle. The
448 nanocoating ~~Tipe E502~~**with alcoholic base** seems to impart no difference on the PNC when

449   it is compared with the uncoated reference. The two have almost the same PNC levels. Since
450   the nanocoating ~~E502~~ probably gets rubbed off completely without providing any resistance,
451   the PNC attains its maximum value (≈ 200 cm^{-3}) soon after the abrasion starts. The standard
452   deviation ranges from 5 to 16 cm^{-3}. For the nanocoating ~~Photocal~~**with PMMA**, the PNC is
453   initially low (≈ 14 cm^{-3}) due to a probable resistance of the nanocoating against abrasion.
454   However, this resistance continues up to a certain point (t= 624 s) after which it may start
455   getting rubbed off. As a result, the PNC starts increasing gradually. It attains the same value
456   as for **the other** nanocoating ~~Tipe E502~~ or the reference towards the end of the abrasion. The
457   standard deviation in the values measured for the nanocoating ~~Photocal~~ **with PMMA** varies
458   from 0.7 to 27 cm^{-3}.

460   *[Place figures 10 (a) (b) here]*

462   In figure 10 (b), the PSD of the emitted aerosol particles is shown. The nanocoating ~~Tipe~~
463   ~~E502~~**with alcoholic base** seems to have no effect on the PSD either except the shift of the
464   size mode towards smaller particle sizes (154 ± 10 nm). The standard deviation in the PSD
465   measured in this case changes from 0.2 to 16 cm^{-3}. The nanocoating ~~Photocal~~ **with PMMA**
466   considerably drops the peak of the PSD curve by a factor of ~ 30 rendering the particle
467   emission totally insignificant. The standard deviation measured here is 8 cm^{-3} maximum.

469   In figure 11 (a), effect of increasing F_N has been shown on a 4 layered ~~Photocal~~ **nanocoating**
470   ~~sample~~**with PMMA**. The abrasion commences at t= 240 s and ends at t= 840 s. For a clear
471   view of the PNC, between t= 240 s and t= 480 s, a zoomed view in figure 11 (a1) is also
472   shown. The PNC increases with normal load. The same pattern continues in figure 11 (b) for
473   a 4 layered ~~Tipe E502~~**nanocoating** ~~sample~~ **with the alcoholic base** too. While measuring the
474   PSD ~~in case of Photocal~~**for the nanocoating with PMMA**, the ~~SMPS and APS~~**PSD** showed
475   very low concentrations which were even close to their particle detection thresholds. Hence,
476   the two particle sizers were not employed further. But for ~~Tipe E502~~**the nanocoating with**
477   **alcoholic base**, there were no such problems. ~~Thus, t~~**T**he PSD ~~for Tipe E502~~**in this case** is
478   shown in figure 11 (c). Three unimodal distributions with increasing size modes (i.e. 154 nm
479   to 274 nm to 365 nm) and increasing concentration peaks can be seen for increasing normal
480   loads.

482   *[Place figures 11 (a), (a1), (b) and (c) here]*

484   The number of layers also has a substantial effect on PNC. The figure 12 demonstrates this
485   effect where two samples, having 2 and 4 layers of ~~Photocal~~**the nanocoating with PMMA**,
486   are tested for F_N= 6 N. The abrasion commences at t= 240 s and ends at t= 840 s. The PNC is
487   always lower when ~~a~~ 4 layer~~ed sample~~ **of the nanocoating** (std. deviation: 2 to 27 cm^{-3}) is
488   abraded as compared to the 2 layer~~ed one~~ (std. deviation: 13 to 37 cm^{-3}) or an uncoated
489   reference. Both sets of layers seem to provide resistance towards abrasion. However, in the
490   case of ~~Tipe E502~~**the nanocoating with alcoholic base**, both 2 and 4 layer~~ed samples~~ ha~~d~~**ve**
491   similar PNC.

493   *[Place figure 12 here]*

495   The SEM observations of the 4 layered ~~Photocal sample~~**nanocoating with PMMA** were also
496   done at the end of the abrasion. The figure 13 shows the observation. An unabraded coated
497   surface (marked A) had an average Ti content of $\sim 12\%$ (in mass). For the abraded part

498 (marked B), the average Ti content lowers down to ∼0% (in mass), thus, completely
499 exposing the brick surface.
500
501 *[Place figure 13 here]*
502
503 Hence, a 4 layered ~~sample of Photocal~~**nanocating with PMMA** has performed remarkably
504 well as compared to its 2 layered counterpart or ~~Tipe E502~~**the other nanocoating**, including
505 its both 2 and 4 layer~~sed of nanocoating~~**samples**. Considering this observation, some 4
506 layered samples of ~~Photocal~~ **of the nanocoating with PMMA** were also exposed to the
507 artificial accelerated weathering prior to their abrasion. In figures 14 (a)-(e), one may see a
508 deteriorating effect of the weathering ~~of the 4 layered Photocal sample~~. A continuous and
509 integrated form of the nonweathered nanocoat~~ed~~**ing** ~~sample~~ can be observed in figure 14 (a).
510 A progressive deterioration of the nanocoating via cracking can be then observed in the
511 successive figures i.e. figures 14 (b), (c), (d) and (e). On the contrary, an uncoated reference
512 ~~sample~~ shows no such effects. The drying stress due to water content evaporation and gradual
513 embrittlement of the polymeric binder present in the nanocoating during its interaction with
514 UV rays result in such a deterioration (White[35], Murray[36], Dufresne *et al.*[37], Hare[38]
515 Tirumkudulu and Russel[39]). The EDS analysis of the weathered nanocoat**ing**~~ed sample~~
516 ~~surfaces~~ via elemental mapping between Ti (contributed by the nancoating) and Ca
517 (contributed by the brick) is shown in figures 14 (f)-(j). In the figure, an almost stagnant Ti
518 content on the surface (average value ∼16.1%) can be observed with an increasing Ca
519 content and hence the exposed surface. One of the major implications of this result can be the
520 shrinkage of nanocoating with weathering.
521
522 *[Place figures 14 (a)-(j) here]*
523
524 The quantification of the TiO_2 nanoparticles emission in the water was carried out at the
525 intervals of 2, 4, 6 and 7 months of weathering. For this 100 ml samples of leachate were
526 taken from the collected runoff water and analyzed using an Inductively Coupled Plasma
527 Mass Spectrometry (ICP-MS). Table 3 shows ICP-MS's operating conditions. We found that
528 the Ti was found to be always below the threshold detection value (= 0.5 μg/l) in the sample
529 volume. This observation leads to the conclusion that despite the deterioration by weathering,
530 the ~~nanocoated sample surfaces are~~**nanocoating is** still strongly bound to resist their leaching
531 into the runoff waters.
532
533 *[Place table 3 here]*
534
535 The weathering was followed by the abrasion~~. of both uncoated reference and nanocoated~~
536 ~~samples of Photocal~~. The figures 15 (a) and (b) show the results of TEM analysis of the
537 sampled aerosol particles, during the first 2 min of abrasion of the 4 and 7 months weathered
538 ~~Photocal samples~~ **nanocoating** under the same sampling conditions. A qualitatively higher
539 deposition of aerosol particles on the mesh grids can be observed in the case of latter. The
540 polydispersed aerosol particles can be observed upon higher magnification. Even though we
541 weren't able to quantify, but a significant amount of free nanoparticles of TiO2 (i.e. Ti mass>
542 90%) was observed when 7 months weathered ~~samples were~~**nanocoating was** abraded
543 (figure 15 (c) (d)). This result differs from the findings of non-weathered nanocoatings and
544 various other studies like Shandilya *et al.*[15], Golanski et al.[23], Göhler *et al.*[29], Shandilya *et*
545 *al.*[33]. Hence, it is of more particular interest. In previously obtained results for non-weathered
546 nanocoatings and other mentioned studies, a large fraction of the emitted aerosols composed
547 of the nanomaterial in the matrix-bound state and not in the free state.

548

550

551   In the figure 15 (e), the variations in the percentages of the three elements- C, Ti and Ca are
552   shown when the weathering duration reaches 7 months from 4 months. A clear effect of the
553   polymer embrittlement can be observed with a drop in the C content from 56% to 12%. This
554   drop directly implies the reduction in the presence of the matrix around the emitted aerosol
555   particles. An increase from 7% to 55% in the Ti content signifies an increase of Ti
556   concentration in the emitted aerosol particles. The exposed surface of the underlying brick,
557   after 7 months of weathering, yields some aerosol particles too upon abrasion. As a result,
558   some aerosol particles from the brick are also observed after 7 months of weathering.
559   Hence, the weathering duration has a direct impact on the size and chemical composition of
560   the aerosol particles.

561

563

564   The figures 16 (a)-(d) show the results on PNC and PSD of the aerosol particles sampled
565   within the volume of the sampling hood. In figures 16 (a) and (b), starting at t= 120 s and
566   continuing until t= 720 s, the abrasion of the uncoated reference ~~samples~~ yielded a constant
567   and weathering duration independent PNC ($\sim$500 cm^{-3}; standard deviation 5$-$16 cm^{-3};
568   repeated thrice). Therefore, the artificial weathering has no apparent effect on emitted aerosol
569   particles from the uncoated reference ~~sample~~. However, in the case of the ~~Photocal~~
570   **nanoacoating**~~samples~~, a clear effect of the weathering duration can be observed as the PNC
571   increases with weathering duration. Except for 6 and 7 months, the nature of its variation
572   with time is also strikingly similar i.e. initial ascension, followed by stagnation, then
573   ascension again, and the final stagnation. For 6 and 7 months ~~weathered samples~~, there is an
574   immediate bump in the concentration as soon as the abrasion starts. This initial bump in the
575   concentration is even higher than that of the reference ~~sample~~. However, after t=360 s, it
576   tends to come back to the **reference**~~same~~ level ~~as that of the reference sample~~. This
577   difference in the nanocoating behavior with respect to the abrasion can be explained on the
578   basis of its removal mechanism during abrasion. Until 4 months of the weathering, the
579   nanocoating is believed to be strong enough to resist its abrasion. As a result, it gets *worn*
580   slowly and hence, the number concentration of the emitted aerosols increases slowly.
581   However, after 6 and 7 months of the weathering, the nanocoating is lumpy (as already seen
582   in the figure 14 (e)) as possibly loosely attached to the brick's surface. As a result, as soon as
583   the abrasion starts, these nanocoating lumps get *uprooted* easily which shows a bump in the
584   number concentration of the emitted aerosol particles. The PSD of the emitted aerosol
585   particles for the reference ~~sample~~ (figure 16 (c)) shows no apparent effect of the weathering
586   (mode alternating between 250 and 350 nm; PNC $\approx$375 cm^{-3}; standard deviation 0.2$-$8 cm^{-3}).
587   In figure 16 (d), the particle size distribution is shown for the ~~Photocal~~ **nanocoat**~~samples~~**ing**
588   that correspond to the first phase during which the EAPNC is stagnant. This figure does not
589   show any curve for 6 and 7 months weather**ing**~~ed test samples~~ because there is no first
590   stagnant phase for them. As one may see clearly, there is an increase in the size mode as well
591   as maximum EAPNC.

592

593   **Emission from the glaze**
594   Contrary to the aerosol particles emission observations in the case of the reinforced bricks
595   and photocatalytic nanocoatings, the two layers **of** glaze~~d wooden samples~~ were found to be
596   non-emissive during their abrasion when F_N= 6 N. The number concentration of the emitted

aerosol particles, obtained using ~~CPC 3775~~**the particle counter**, was always found to be less than 1 cm^{-3}, hence insignificant.

FIGURE LEGENDS:
Figure 1: The original form of Taber 5750 linear abrasion apparatus (b) the replica of the steel bar in aluminum mounted with the strain gauge at top

Figure 2: Experimental set-up (Shandilya *et al.*[31])

Figure 3: Suntest XLS+ weathering chamber

Figure 4: SEM image of the nanostructured alumino-silicate brick (Shandilya *et al.*[33])

Figure 5: TEM analyses of the morphology of the nanoparticles present in **the nanocoating with** (a) ~~Photocal Masonry® –~~**PMMA** and (b) ~~Tipe E502⊕~~**alcoholic base as dispersant** (Shandilya *et al.*[33])

Figure 6: (a) TEM and (b) Elemental composition analysis of NANOBYK-3810

Figure 7: Variation of the total worn mass of the brick with increasing normal load (Shandilya *et al.*[33])

Figure 8: Particle size distribution (PSD) of the emitted aerosol particles as a function of normal load (Shandilya *et al.*[33])

Figure 9: (a) Total emitted aerosol particles number concentration (PNC) of the aerosol particles as a function of normal load (Shandilya *et al.*[34]) (b) Total PNC and PSD mode as a function of tangential load

Figure 10: (a) PNC variation with time (b) PSD of the aerosol particles emitted during the abrasion of 4 ~~layered~~ **layers of the** nanocoating ~~samples~~ under 6 N of normal load (note: all the curves are mean curves obtained from 3 repeated tests) (Shandilya *et al.*[33])

Figure 11: (a) PNC variation with time for 4 layer~~ed~~**s of** ~~Photocal~~ **nanocoating with PMMA** and (b) ~~Tipe E502 sample~~**alcoholic base**; (a1) zoomed view; (c) PSD of the aerosol particles emitted during the abrasion of 4 ~~layered~~ **layers of** ~~Tipe E502 sample~~**nanocoating with alcoholic base** (note: all the curves are mean curves obtained from 3 repeated tests) (Shandilya *et al.*[33])

Figure 12: PNC variation with time for 2 and 4 layer~~ed~~**s of** ~~Photocal samples~~ **nanocoating with PMMA** (note: all the curves are mean curves obtained from 3 repeated tests) (Shandilya *et al.*[33])

Figure 13: SEM image and EDX analysis of the coated and abraded parts of the ~~Photocal~~ **nanocoating with PMMA**~~sample~~; part (A): unabraded coated surface; part (B): abraded (Shandilya *et al.*[33])

Figure 14: Microscopic analysis of progressively deteriorating ~~Photocal sample~~**nanocoating** (Shandilya *et al.*[31])

Figure 15: TEM image of aerosol particles emitted from the abrasion of (a) 4 months and (b) 7 months weathered ~~Photocal~~ **nanocoating** ~~samples~~ (c, d) free nanoparticles emitted from the abrasion of 7 months weathered ~~Photocal samples~~ **nanocoating** (e) Chemical analysis of aerosol particles emitted from the abrasion of 4 and 7 months weathered ~~Photocal samples~~ **nanocoating** (Shandilya et al.[31])

Figure 16: PNC and PSD during the abrasion of weathered reference and ~~Photocal~~ **nanocoating** ~~samples~~. The abrasion takes place for t = 120−720 s in panels (a) and (b). (Shandilya et al.[31])

Table 1: Material properties of the nanostructured alumino-silicate brick

Table 2: Average aerosol particle size of the sampled aerosol particles at different values of F_N

Table 3: Operating conditions of ICP-MS

DISCUSSION:

In the present article, an experimental investigation of the nanosafety-by-design of commercial nanostructured products is presented. The nanosafety-by-design of any product can be studied in terms of its PNC and PSD when it is subjected to mechanical stresses and environmental weathering. The products chosen for the study are alumino-silicate brick reinforced with TiO_2 nanoparticles**, glaze with CeO_2 nanoparticles** and **photocatalytic** nanocoatings with TiO_2 nanoparticles ~~i.e. Photocal Masonry® & Tipe® E502~~. These products are easily accessible to the customers in the commercial market and well associated with their daily lives. Therefore, their investigation towards their nanosafety-by-design is crucial.

During the abrasion of the nanostructured brick, a critical role of the normal load, F_N, was observed in terms of PNC and PSD. With an increase in its value, the average size of the emitted aerosol particles increases too. When $F_N \leq 10.5$ N, the emitted aerosol particles are mainly composed of smaller sized aerosol particles (< 365 nm). Beyond 10.5 N, more and bigger-sized aerosol particles start being generated. In the latter case, most of the emitted aerosol particles have more tendency to deposit on the surface as debris rather than to aerosolize. Hence, after increasing initially, the PNC either decreases or attains a constant value beyond a critical value. Considering such a critical role, $F_N = 10.5$ N can be termed as *critical normal load* value of F_N i.e. $(F_N)_{cr}$. The authors believe that the value of $(F_N)_{cr}$ is exclusively material dependent. However, further tests are still to be carried out to confirm this hypothesis.

It is well known that any solid surface is composed of the microscopic identities or waviness which induce roughness to it. They are called surface *asperities*. Each individual asperity is in contact with each other. Considering this fact, one may hypothesize that when the value of F_N is lower than $(F_N)_{cr}$, the fracturing of the surface asperities takes place in such a way that it favors the generation of lower wear mass and smaller-sized particles. Such a case can be imagined if the fracture passes through the asperity, thus, disintegrating it in a number of smaller fragments. This can be compared with a *trans-granular fracture* in crystalline solids. But when F_N is higher than $(F_N)_{cr}$, the fracturing of the surface asperities take place in such a way that it favors the generation of higher wear mass and bigger-sized aerosol particles. The concentration of the smaller-sized aerosol appears to either remain constant or decrease. Such

697 a case can be imagined if the fracture passes along the boundary of the asperities, thus,
698 cutting them out of the surface. This can be compared with an *inter-granular fracture* in
699 crystalline solids.
700
701 Opposite to the brittle fracture behavior of the brick surface asperities, the porous fibrous
702 nature of the glazed wooden surfaces has a porosity dependent emission behavior, as
703 explained by Shandilya *et al.*[40]. The non emissivity of these test samples is in direct
704 agreement with the simulated insignificant emissions obtained in Shandilya *et al.*[41].
705
706 During the abrasion of the two non-weathered photocatalytic nanocoatings, we found that the
707 emitted ENM are never in their pristine form, but rather embedded inside the dispersant
708 matrix of the nanocoating. Based on the results, we also conclude that one may achieve the
709 reduction in the PNC or ENM release from the nanocoatings by following either of the two or
710 both remedies: (a) selection of a product having good interfacial adhesion with the substrate;
711 (b) increase in the number of coating layers on the substrate. A coating on the surface is
712 believed to act like a resistor to the externally applied mechanical stress which reduces its net
713 impact. By increasing the number of the coating layers, the resistance effect further improves.
714 Also, the surface energy, one of the key parameters affecting PNC, as identified by Shandilya
715 *et al.*[40], lowers with increasing number of the layers. Since the surface energy is directly
716 proportional to the number of the released particles (Shandilya *et al.*[41]), therefore, its
717 lowering leads to the reduction in PNC.
718
719 The environmental weathering, simulated via accelerated artificial weathering, was found to
720 have a strong effect on the changes in the material properties. Hence, it also plays an
721 important role in deciding the nature and quantity of PNC or released ENM. In the literature
722 as well as in the present work, the environmental weathering is observed to bring
723 deterioration of the product matrix. However, the extent of this deterioration depends upon
724 the type of the matrix and duration of the weathering. During the course of the experiments, it
725 is constantly observed that the occurrence of the ENM inside a matrix, during emission,
726 continues until the matrix has a high interfacial shear strength value. With increasing
727 weathering duration, there is a step-wise structural deterioration of the nanocoating which
728 leads to the decrease in the interfacial shear strength between the matrix and the ENM. As a
729 result, the emission of free ENM starts occurring. In such a case, if there is a flow of water
730 over the surface, known as runoff, the leaching of these ENM in the runoff water is highly
731 probable (although not observed in the present case but it is still probable for higher
732 weathering durations). With a high specific surface area, these free ENM now accentuate a
733 potential risk in terms of *nano-toxicity*.
734
735 ~~One of the~~The ~~Unique Selling Proposition~~significance of our contribution towards a
736 Nanosafety-by-design approach in studying the emission of nanoparticles during their
737 product lifetime is that it focuses on finding a weathering duration threshold beyond which
738 the chosen nanocoating has exceeded its nanosafe lifetime. (In the present case, it's 4 months
739 of accelerated weathering.) This is done through a continuous monitoring of the in-process
740 nanocoating state which allowed us to note the exact duration in which the nanocoating
741 started to deteriorate. This is the feature which distinguishes it from previous scientific
742 studies as they deal with the concept of the environmental weathering by applying it on a test
743 sample for a predetermined duration with no in-process monitoring of the ongoing
744 weathering. The approach chosen in the study presented here allows for quantitatively
745 comparing experimentally measured nanosafety thresholds (i.e. nanosafe lifetimes) of

different –but similar- nanoproducts (under similar accelerated life conditions). It is thus the first step developing products on a Nanosafety-by-design basis.

A major limitation of the protocol presented for the ENM aerosols characterization is that a fraction of these ENM aerosols get lost before they can be characterized for their size and number. Such a loss can be attributed to various phenomena associated with the aerosol dynamics like sedimentation, diffusion, turbulence in the air flow, inertial deposition etc. which act on an aerosol particle simultaneously as soon as it gets emitted. This loss is a direct function of the aerosol particle size. This aspect has been considered in some previous publications like Shandilya *et al.*[31], Shandilya *et al.*[33], Shandilya *et al.*[34]. However, the consideration approach has been reactive in these studies i.e. calculations were done to approximately estimate the loss and the final experimental results were modified on the basis of the calculation results. In the case of a preemptive approach, the experimental set-up should be modified accordingly to minimize the loss so that a complete and accurate quantitative study of the emitted aerosol particles can be done. This shall be the focus of our future studies.

DISCLOSURE:
The authors have nothing to disclose.

REFERENCES:
1. Potocnick, J., European Commission Recommendation on the definition of nanomaterial. **2011/696/EU**, ~~Oct~~ (2011).

2. Oberdorster, G., Oberdorster, E., Oberdorster, J. Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. Environmental Health Perspectives, **113 (7)**, 823-839, **doi: 10.1289/ehp.7339,** (2005).

3. Le Bihan, O., Shandilya, N., Gheerardyn, L., Guillon, O., Dore, E., Morgeneyer, M. Investigation of the Release of Particles from a Nanocoated Product. Advances in Nanoparticles, **2 (1)**, 39−44, **doi: 10.4236/anp.2013.21008,** (2013).

4. Houdy, P., Lahmani, M., Marano, F. Nanoethics and Nanotoxicology. Springer, Heidelberg, Germany, 1st edition, (2011).

5. Kulkarni, P., Baron, P. A., Willeke, K. Aerosol Measurement: Principle, Techniques and Applications. John Wiley and Sons, Hoboken, NJ, USA, 3rd edition, (2011).

6. Hsu, L.Y., Chein, H.M. Evaluation of nanoparticle emission for TiO_2 nanopowder coating materials. Nanoparticle Research, **9 (1)**, 157–163, **doi: 10.1007/s11051-006-9185-3,** (2007).

7. Maynard, A.D. Safe handling of nanotechnology. Nature, **444 (1)**, 267-269, **doi: 10.1038/444267a,** (2006).

8. Shatkin, J.A. *et al*. Nano risk analysis: advancing the science for nanomaterials risk management. Risk Analysis, **30 (11)**, 1680-1687, **doi: 10.1111/j.1539-6924.2010.01493.x.,** (2011).

9. Göhler, D., Nogowski, A., Fiala, P., Stintz, M. Nanoparticle release from nanocomposites due to mechanical treatment at two stages of the life-cycle. Phys Conf Ser, **429 012045**, ~~DOI~~doi: 10.1088/1742-6596/429/1/012045, (2013).

10. Allen, N.S. *et al.*~~, Edge, M., Corrales, T., Childs, A., Liauw, C.M., Catalina, F., Peinado, C., Minihan, A., Aldcroft, D.~~ Ageing and stabilisation of filled polymers: an overview. Polymer Degradation and Stability, **61 (2)**, 183-199, **doi: 10.1016/S0141-3910(97)00114-6,** (2004).

11. Allen, N.S. ~~, Edge, M., Ortega, A., Sandoval, G., Liauw, C.M., Verran, J., Stratton, J., McIntyre, R.B~~*et al.* Degradation and stabilisation of polymers and coatings: nano versus pigmentary titania particles. Polymer Degradation and Stability, **85 (3)**, 927-946, **doi: 10.1016/j.polymdegradstab.2003.09.024,** (2004).

12. Al-Kattan, A. *et al.*~~, Wichser, A., Vonbank, R., Brunner, S., Ulrich, A., Zuind, S., Nowack B.~~ Release of TiO_2 from paints containing pigment-TiO_2 or nano-TiO_2 by weathering. Environmental Science: Processes & Impacts, **15 (12)**, 2186-2193, **doi: 10.1039/C3EM00331K,** (2013).

13. Kaegi, R. ~~, Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M~~*et al*. Synthetic TiO_2 nanoparticle emission from exterior facades into the aquatic environment. Environmental Pollution. **156 (2)**, 233- 239, 2008.

14. Hirth, S., Cena, L., Cox, G., Tomovic, Z., Peters, T., Wohlleben, W. Scenarios and methods that induce protruding or released CNTs after degradation of nanocomposite materials. Nanoparticle Research, **15 (2)**, 1504-1518, **doi: 10.1007%2Fs11051-013-1504-x,** (2013).

15. Shandilya, N., Le Bihan, O., Morgeneyer, M. A review on the study of the generation of (nano-) particles aerosols during the mechanical solicitation of materials. J. Nanomaterials, No. **289108**, **doi: 10.1155/2014/289108**, (2014).

16. Wohlleben, W. *et al.*~~, Brill, S., Meier, M.W., Mertler, M., Cox, G., Hirth, S., von Vacano, B., Strauss, V., Treumann, S., Wiench, K., Ma Hock, L., Landsiedel, R.~~ On the lifecycle of nanocomposites: comparing released fragments and their in vivo hazards from three release mechanisms and four nanocomposites. Small, **7 (16)**, 2384-2395, **doi: 10.1002/smll.201002054,** (2011).

17. Bouillard, J. X.~~, R'Mili, B., Moranviller, D., Vignes, A., Le Bihan, O., Ustache, A., Bomfim, J. A. S., Frejafon, E., Fleury, D~~ *et al.*~~.~~ Nanosafety by design: risks from nanocomposite/nano waste combustion. Journal of Nanoparticle Research, **15 (1)**, 1519-1529, **doi: 10.1007/s11051-013-1519-3,** (2013).

18. Ounoughene, G. ~~, Le Bihan, O., Chivas-Joly, C., Motzkus, C., Longuet, C., Debray, B., Joubert, A., Le Coq, L., Lopez Cuesta, J.M~~*et al*. Behavior and fate of Halloysite Nanotubes (HNTs) when incinerating PA6/HNTs nanocomposite. Environmental Science & Technology, **49 (9)**, 5450-5457, **doi: 10.1021/es505674j,** (2015).

19. Morose, G. The 5 principles of "Design for Safer Nanotechnology". Journal of Cleaner Production, **18 (3)**, 285–289, **doi: 10.1016/j.jclepro.2009.10.001,** (2010).

20. ASTM International, Standard test method for the abrasion of organic coatings by the Taber abradant. **ASTM D4060**, (2007**).**

21. ASTM International, Standard test methods for dry abrasion mar resistance of high gloss coatings. **ASTM D6037**, (1996**).**

22. ASTM International, Standard test method for resistance of transparent plastics to surface abrasion. **ASTM D1044**, (2008**).**

23. Golanski, L., Guiot, A., Pras, M., Malarde, M., Tardif, F. Release-ability of nano fillers from different nanomaterials (toward the acceptability of nanoproduct). Nanoparticle Research, **14 (1)**, ~~article~~ 962-**970**, **doi: 10.1007/s11051-012-0962-x,** (2012).

24. Vorbau, M., Hillemann, L., Stintz, M. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. Journal of Aerosol Science, **40 (3)**, 209–217, **doi: 10.1016/j.jaerosci.2008.10.006,** (2009).

25. Hassan, M.M., Dylla, H., Mohammad, L.N., Rupnow, T. Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement. Construction and Building Materials, **24 (8)**, 1456–1461, **doi: 10.1016/j.conbuildmat.2010.01.009,** (2010).

26. Morgeneyer, M., Shandilya, N., Chen, Y.M., Le Bihan, O. Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation. Chemical Engineering Research & Design, **93 (1)**, 251−256, **doi: 10.1016/j.cherd.2014.04.029,** (2015).

27. Morgeneyer, M., Le Bihan, O., Ustache, A., Aguerre Chariol, O. Experimental study of the aerosolization of fine alumina particles from bulk by a vortex shaker. Powder Technology, **246 (1)**, 583-589, **doi: 10.1016/j.powtec.2013.05.040,** (2013).

28. Le Bihan, O., Morgeneyer, M., Shandilya, N., Aguerre Chariol, O., Bressot, C. Chapt. 7, In Handbook of Nanosafety: Measurement, Exposure and Toxicology. (Eds.) Vogel, U., Savolainen, K., Wu, Q., Van Tongeren, M., Brouwer, D., Berges, M. Academic Press, San Diego, CA, (2014).

29. Göhler, D., Stintz, M., Hillemann, L., Vorbau, M. Characterization of nanoparticle release from surface coatings by the simulation of a sanding process. Annals of Occupational Hygiene, **54 (6)**, 615−624, **doi: 10.1093/annhyg/meq053,** (2010).

30. R'mili, B., Le Bihan, O., Dutouquet, C., Aguerre Charriol, O., Frejafon, E. Sampling by TEM grid filtration. Aerosol Science and Technology, **47 (7)**, 767−775, **doi: 10.1080/02786826.2013.789478,** (2013).

31. Shandilya, N., Le Bihan, O., Bressot, C., Morgeneyer, M. Emission of Titanium Dioxide Nanoparticles from Building Materials to the Environment by Wear and Weather. Environmental Science and Technology, **49 (4)**, 2163−2170, **doi: 10.1021/es504710p,** (2015).

32. AFNOR, Paints and varnishes − Methods of exposure to laboratory light sources − Part 1: General guidance. **ISO 16474-1**, (2012).

33. Shandilya, N., Le Bihan, O., Bressot, C., Morgeneyer, M. Evaluation of the particle aerosolization from n-TiO₂ photocatalytic nanocoatings under abrasion, J. Nanomaterials, No. **185080**, (2014).

34. Shandilya, N., Le Bihan, O., Morgeneyer, M. Effect of the Normal Load on the release of aerosol wear particles during abrasion. Tribology Letters, **55 (2)**, 227-234, **doi: 10.1007%2Fs11249-014-0351-y,** (2014**).**

35. White, L. R. Capillary rise in powders. J. Colloid Interface Science, **90 (2)**, 536−538, **doi:** 10.1016/0021-9797(82)90319-8, (1982).

36. Murray, M. Cracking in coatings from colloidal dispersions: An industrial perspective. Proceedings Rideal Lecture, London, April 20, 2009.

    http://www.soci.org/~/media/Files/Conference%20Downloads/2009/Rideal%20Lectures%20Apr%2009/Murray.ashx

37. Dufresne, E.R. ~~, Corwin, E.I., Greenblatt, N.A., Ashmore, J., Wang, D.Y., Dinsmore, A.D., Cheng, J.X., Xie, X.S., Hutchinson, J.W., Weitz, D. A~~*et al*. Flow and fracture in drying nanoparticle suspensions, Physics Review Letters, **91**, No. 224501, **doi: 10.1103/PhysRevLett.91.224501,** (2003).

38. Hare, C.H. The degradation of coatings by ultraviolet light and electromagnetic radiation, J. Protective Coatings and Linings, (1992)

    http://www.q-lab.com/documents/public/70ccb209-bf41-4da0-bb80-964d597fc728.pdf

39. Tirumkudulu, M.S., Russel, W.B. Cracking in drying latex films, Langmuir, **21 (11)**, 4938−4948, **doi: 10.1021/la048298k,** (2005).

40. Shandilya, N., Morgeneyer, M., Le Bihan, O. First development to model aerosol emission from solid surfaces subjected to mechanical stresses: I. Development and results. Journal of Aerosol Science, 2015 (submitted)

41. Shandilya, N., Morgeneyer, M., Le Bihan, O. First development to model aerosol emission from solid surfaces subjected to mechanical stresses: II. Experiment-Theory comparison, simulation and sensibility analysis. Journal of Aerosol Science, 2015 (submitted)