PROJECT FINAL REPORT
Final publishable summary

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Declaration by the project coordinator

I, as co-ordinator of this project and in line with my obligations as stated in Article II.2.3 of the Grant Agreement declare that:

- The attached periodic report represents an accurate description of the work carried out in this project for this reporting period;

- The project (tick as appropriate):

  ☒ has fully achieved its objectives and technical goals for the period;
  ☐ has achieved most of its objectives and technical goals for the period with relatively minor deviations[1];
  ☐ has failed to achieve critical objectives and/or is not at all on schedule.

- The public Website is up to date.

- To my best knowledge, the financial statements which are being submitted as part of this report are in line with the actual work carried out and are consistent with the report on the resources used for the project (section 3.6) and if applicable with the certificate on financial statement.

- All beneficiaries, in particular non-profit public bodies, secondary and higher education establishments, research organisations and SMEs, have declared to have verified their legal status. Any changes have been reported under section 5 (Project Management) in accordance with Article II.3.f of the Grant Agreement.

Name of Coordinator: Dr Luana GOLANSKI..

Date: 28 August 2013

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[1] If either of these boxes is ticked, the report should reflect these and any remedial actions taken.

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1. PUBLISHABLE SUMMARY

1.1. Summary of NanoHOUSE project (M1 – M42)

NanoHouse project contributed to the development of appropriate solutions for the use of safe, sustainable and competitive *nano-based paints* – ENPs containingpaint) - through their whole life cycle. To that end, four main strategic innovations are developed:

1.Life Cycle Thinking applied to TiO2, Ag and SiO2 ENPs containing paint, by identifying data gaps and lacks of knowledge considering Environmental Health & Safety issues.

Life cycle thinking (LCT) provides a holistic perspective on opportunities and risks. Life cycle thinking shows that the integration of ENP in façade coatings could gradually improve functions and could have little influence on environmental performance. Win-win situation: LCT helps to identify opportunities and lead to decisions, which may improve environmental performance, image, and economic benefits.

2.Identification of ENPs sources and quantification of the released ENPs during the use phase, post application/service life, and final disposal of nano-based paints.

The ENP source emission understanding is a key point for making safer painting products. Realistic and critical scenarios are implemented in order to test ENP release from painting products. Under hard abrasion and leaching: ENP's are mainly released embedded into the matrix paint or in agglomerate form. Very few single ENP's are released from paints. Source emission is a key point of the ENP release issue for the market and the social acceptance of nano products.

3.Environmental and toxicological studies

.Evaluation of the environmental and the toxicological behaviour/effects of the released ENPs from 'aged *nano-based paints* by comparison with the pristine ENPs.

-Studying the mechanisms of release and environmental fate of ENP is essential for assessing their risks for the environment & human health. From 10 to 90% of the ENP's mass could be transferred through sand depending on their nature and the sand solution chemistry. Only small amount of ENP are released from paints during weathering. The released ENP behaviour is observed to be different compared to the pristine ENP. Exposure of crop plants to ENP does not lead to phytotoxicity symptoms but the bioaccumulation of ENPs in edible parts may lead to their entry in the food chain.

-Toxicity of nano based paints- Nanoparticles in paint represent a complex type of exposure; they interact with the matrix of the paint and age during their lifetime. Both complex cell cultures-mimicking real life-and in vivo tests are performed investigating acute and repeated dosing. Pristine particles show some toxic effects, no significant toxicological changes were observed when they were embedded in a complex paint matrix. The type and characteristics of the material remains important in evaluating its safety.

4. Safe-by-design approaches to overcome ENP release issues

Release of Ag and TiO2 ENPs was insignificant and only very little release of free SiO2 ENPs was observed by leaching test (i.e. wet route) and abrasion studies (i.e. dry route). Nanoparticles release is influenced by the binder: new formulations can reduce the release of nanoparticles.

5. End of life strategies- Nanowaste management

The quantification of generated volumes is the first step of the nanowaste management. Leaching tests applied to paint debris simulate a landfill scenario to provide information about the ENPs release. These first experiments represent a significant advancement towards sustainable end of life solution of solid nanowaste. Nanoparticles release form paint debris is influenced by the binder: new formulations can reduce the release of nanoparticles.

NanoHouse outputs address economic and strategic activities participating to the development of sustainable and competitive nanoproducts:

1. The Life Cycle Thinking will contribute to identify the likely exposure pathways and potential targets(e.g user, consumers…), then reinforce sustainability of the product
2. Sources inventory data for nanoproducts (paints and coatings) opens the way to Nanoproducts technical certification and Responsible Label
3.Behaviour study of 'released nanoparticles' into water, solids and plants allows for innovations to detect nanoparticles into the environment, and then contributes to sustainable industrial policy.
4. Behaviour study of 'released nanoparticles' into human body and immunotoxicity offers new hazard approach contributing to Public Health and Safety recommendations for nanomaterials
5. Waste management of nanoproducts proposes pragmatic solutions for the end of life treatment of the paints: incineration, disposal into the landfill, and then contributes to the development of

nanoproducts policies and regulations at the European level.
According to the paints manufacturers, there is an urgent need to develop new specific standard for nanoparticles containing products. In particular, standard methods for the characterization of nanoparticle release are currently not available. The experimental work performed in Nanohouse project on the quantification of the released sources of ENPs allowed to develop experimental protocols able to assess nanoparticles release from paints under use and at end life cycle that could be recommended as standards.

2. PROJECT CONTEXT AND OBJECTIVES

2.1. WP01- Life Cycle Thinking

We apply Life Cycle Thinking (LCT) on ENP enhanced façade coatings in order to investigate:

- benefits that could be achieved
- potential risks

The LCT considers:

- the whole life cycle of a product (production, use, disposal)
- all components of the product, not only ENP

In NanoHouse the LCT involves:

- qualitative life cycle to identify and describe all the relevant aspects of a product such as the design, potential benefits and what happens with the product during its life cycle
- quantitative life cycle (Life Cycle Assessment, LCA) to compare the environmental performance of ENP enhanced façade coatings to similar conventional façade coatings without ENP.

2.2. WP02- Sources identification

*The aim of the WP2 was the i*dentification of ENPs sources and quantification of the released ENPs during the use phase, post application/service life, and final disposal of nano-based paints. Realistic and critical scenarios were implemented in order to test ENP release from painting products and different paints tested. Based on ENPs results release from paint during post-application of paint in dry and wet conditions a conceptual exposure scenario for humans and workers for the three paint products studied in NanoHOUSE was developed. The fabrication process of ‘’aged ENPs’’ as released from the paints in high quantity was selected and than delivered to partners of WP3 and WP4 for environmental fate and toxicological studies by comparison to the pristine ENP’s.

2.3. WP03- Environmental fate

This work package WP3 had the aim to investigate the reactions of released ENPs in water and the soil-plant system. These are the two major compartments that ENP encounter first when released from the outside of buildings. The particles released under natural weather conditions were characterized and their further fata in water was investigated and compared to the behavior of the pristine particles. Also plant uptake of both pristine and aged particles was investigated. For the assessment of the transport of ENP in soils labeled ENP were developed and then used in soil transport studies. The main innovative aspect of WP3 is that the environmental behavior of actually released ENPs is studied. The work thus extends beyond the current research, which focuses almost exclusively on pristine ENP received directly from producers or synthesized in the laboratory. In NanoHouse the actually released ENPs from paints are compared to pristine ENPs. This will allow relating the existing knowledge to the new results obtained in NanoHouse.

2.4. WP04- Hazard characterization

The mechanisms of action of fine and ultrafine particles on the human health are not yet fully understood. The objectives of WP4 were to focus on processes such as translocation, changes in the cell-layer, oxidative stress, pulmonary (and systemic) inflammation using the pristine particles, the whole commercial mixture (to be used to apply a coating), the “artificially aged” particles and the aged mixture of coating components. The first two materials (from the suppliers of the “new” particle), available during the first year of the project were used to run preliminary test and to validate all methods using particulate matter. The aged materials available later on in the project were used to complete all toxicity – hazard – testing.

2.5. WP05- Safer use and waste management

As ENPs containing products may, similarly to other types of materials and products, inevitably come to the end of their useful life, ENPs could potentially enter the waste stream and find their way into the environment. The main objective of WP5 was to investigate how paint waste containing ENPs may be disposed in landfill, or treated by thermal process / incineration, and to evaluate whether and how ENPs may unintentionally enter into the environment through management of nanowaste. The WP5 was structured in different tasks aimed at evaluating properly methods for end of life of ENPs containing paints, at providing new information and data to paint industry for a suitable waste policies and safety guidelines, and at supporting safer-by-design strategy, e.g. new paint formulation with a reduced release of ENPs.

2.6. WP06- Project dissemination, ethics and nanorisks issues

Focusing on innovation societal issues like life cycle thinking, nanoparticles release, potential toxicity of the aged paint containing nanoparticles, nanowaste management and safer design recommendations for paint manufacturers, NanoHouse potential impact could be summarize in 5 points:

1) During use phase, the nanoparticles seem to be stably attached to the coating, but the production and recycling phases could be hot spots for unintended release.
2) For normal use, release of free or agglomerated nanoparticles is negligible**.** Under hard abrasion and leaching tests, nanoparticles are mainly released embedded into the matrix paint or in form of agglomerates.
3) The pristine nanoparticles examined in this project showed some toxicity at elevated concentrations. After aging, paints containing these nanoparticles show no significant toxicological changes compared with pristine nanoparticles.
4) Simulation of landfill conditions showed insignificant release of nanoparticles, geomembranes are able to block potential release and there is no evidence of nanoparticles emitted with fumes during incineration experiment.
5) Finally, testing different paint formulations for safer design shows that it is possible to reduce the nanoparticles release during the abrasion and leaching tests by adjusting the properties of the binder in combination with common pigment.

2.7. WP07- Project management and IPR

The NanoHOUSE consortium is made of 9 partners (5 Research Organizations, 1 SME, 3 industrial companies) from 4 different countries. A multidisciplinary approach is set forth to investigate ENPs impact on human health during ENPs life cycle, ranging from ENPs release from the nanoproduct to the disposal of ENPs-based products. The ambitious objectives require a high-quality management structure and a coherent organization, able to support the various tasks of the project, address risks and minimise their effects on the project. Therefore the NanoHOUSE project is structured and organised according to the international best practices. WP7 will strive to planning the research project, monitoring the execution of the project, and managing the dissemination and use of its results.

3. DESCRIPTION OF THE MAIN S/T RESULTS / FOREGROUNDS

3.1. WP01- Life Cycle Thinking

We apply Life Cycle Thinking (LCT) on ENP enhanced façade coatings in order to investigate benefits that could be achieved and the potential risks.

In NanoHouse the LCT involves a qualitative life cycle to identify and describe all the relevant aspects of a product such as the design, potential benefits and what happens with the product during its life cycle and a quantitative life cycle (LCA) to compare the environmental performance of ENP enhanced façade coatings to similar conventional façade coatings without ENP.

Through the combination of all results (WP2, WP3, WP4, WP5), a set of hotspots were identified and recommendations for stakeholders were given accordingly:

1. Qualitative Life cycle

Qualitative Life Cycle is based on literature reviews, a survey, and a questionnaire for project partners and project partner results and provides an overview on:

The potential benefits of ENP enhanced façade coatings

First market data on the use of nanoparticles in paint and coatings related to the building field was studied. Then the ENP and facadecoatings to be tested in the project were chosen.

In the second part of the literature review was investigated the state of the art on the potential benefits of nanomaterials (functions) in façade coatings, the type of nanomaterials and their related functions and the technical challenges and the different design modes. The objective was to expand the focus of the project NanoHouse from TiO2, SiO2 and Ag to other ENP that might be relevant to façade coatings and describe the state of the art of unintended release of ENP during the product life cycle.

Hot spots for potential unintended release of ENP during the life cycle stages of façade coating

The objective was to illustrate the environmental health and safety (EHS) impacts of façade coatings based on nanomaterials during the product life cycle and to rieview the state of the art of ENP effects on EHS, for instance:

o Environment: (1) the indication for hazardous effects, (2) dissolution in water increases/ decreases toxic effects, (3) tendency for agglomeration or sedimentation, (4) fate during waste water treatment, and (5) stability during incineration

o Health: (1) acute toxicity, (2) chronic toxicity, (3) impairment of DNA, (4) crossing and damaging of tissue barriers, (5) brain damage and translocation and effects of ENP in the (6) skin, (7) gastrointestinal or (8) respiratory tract.

Also a Survey was performed to obtain an overview about potential benefits and hotpots directly from the paint industry.

Results from qualitative life cycle:

a. In the NanoHouse Survey the most mentioned potential functional benefits of ENP enhanced façade coatings (SiO2, TiO2, Ag) are:

o "easy to clean"
o Antimicrobial
o UV protection
o scratch resistance

b. It also was shown that ENP improve gradually (25%), notably (25%) and showed no improvements (50%) of the functionalities of the nano containing façade coating compared with traditional paints

c. A lack of information about nano waste management was identified as well

d. The improvement of the environmental performance is not in the focus of innovation based on ENP.
e. From the literature review was observed that some ENP might affect the human health less severely than they might affect the environment, whereas the case for others is vice versa (Som et al. 2011 and Som et al. 2012)
f. Mechanisms that may lead to a nano-functionality are less understood, due to ENPs high reactivity and variability make difficult to understand mechanism of functionality and prediction of midterm behavior and stability of ENP in materials
g. The minimization of unintended released through design and all steps (quality and safety) should be carried out hand in hand
h. Integration the ENP into the coating material as tightly as possible to ensure the stability of the suspension, a long lasting performance and avoid a loss in the functionality of the coating. Therefore fluids or paste-like formulations instead of powder are better to handle and to avoid potential risks.
i. Hot spots for potential unintended release of ENP were identified:
o No release of high quantities of ENP is observed during the use phase of façade coatings (see experimental part of NanoHouse)
o However, inhalation of airborne ENP during production or recycling of construction material may be an issue for occupational health
o Furthermore, ENP release to technosphere and environmental compartments could be expected in the long term by disposing industrial waste, leftovers and incineration residues on landfills and not pre-treated waste water from the industries to water bodies

2 Quantitative life cycle (LCA)

LCA compares the environmental performance (resource consumption, waste production) of ENP enhanced façade coatings with similar conventional products.

a. **Goal and scope definition**: The appropriate functional unit ((here, 1m2 of wall over a period of 80 years, i.e. the typical life-time of a modern building) and system boundaries are defined
b. **Life cycle inventory analysis (LCI)**: Identifies and quantifies “Input” (resource consumption) and “Outputs” (waste production, emissions) of the façade coatings during the whole life cycle
c. **Life cycle impact assessment (LCIA)**:Uses information on ENP emissions and toxicity
d. **Interpretation**: It shows under what conditions the ENPs should be used, what benefits they bring and it provides information for decision making

Results from LCA

Literature shows so far only few LCA studies of ENP. And still, a relevant part of these few studies is based on functional units of one weight unit, what might not be appropriate to compare specific functionalities of ENP enhanced products with traditional (i.e. conventional) products. Moreover, only about one third of these studies take into account the complete life cycle.

The process takes into account not only changes in life-span of these pain formulations but also eventual releases of ENPs due to weathering processes. The respective results will be published in the summer of 2013 – in a scientific publication – as well as in Deliverables D1.4 and D1.5.

3.2. WP02- Sources identification

Task 2.1. It was planned to work in task 2.1 to identify nanoparticle release sources in outdoor and indoor applications: via the ‘’wet route’’ (task 2.1.1) and nanoparticle release via the ‘’dry route’’ (task 2.1.2). ***Realistic and critical scenarios are implemented in order to test ENP release from painting products.*** An important experimental work was carried out to determine how ENPs might be released from paint coatings during the use phase and post application of nano-based paint, as well as during their final disposal in landfill. Non-commercialized facade paints were formulated with and without TiO2, SiO2 and Ag ENPs. Paints were applied to suitable fibre-cement support. Fibre-cement was chosen as the coatings adhered well to this material, and it offers an exterior facade-like appearance. Realistic and critical scenarios were implemented in order to test abrasion-induced ENP release from painting products into the air before and after UV aging and accelerated artificial weathering scenarios (EN ISO 10686). For abrasion studies of painted surfaces the standardized Taber Abrader method was used. The abrasion conditions conform standard NF EN ISO 7784-1 and NF EN ISO 7784-2 were chosen. ***Protocol used for ENPs release into the air*** *Taber test (EN ISO 7784-2) widely used to simulate wear of the coatings was adapted with the appropriate methodology to assess the potential ENPs release induced by abrasion in air. Other mechanical stresses representative of critical operations like scratching were applied as well.* 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. This test reproduces the aging effect induced by a mechanical friction. It was observed that the amount of released particles depends on: the intensity of the mechanical stress, the paint formulation and the aging treatment. For normal use, release of free or agglomerated ENPs is negligible. For critical conditions the amount of released ENPs in air depends on: the intensity of the mechanical stress, the paint formulation: pigment volume concentration and binder amount, the aging treatment. Under hard abrasion, pieces of paints containing ENP embedded into the matrix are more likely to be removed. No free or agglomerated ENP were observed for the paints containing Ag or TiO2. Paint containing nanoSiO2 released very few free and agglomerated ENP. While same paint formulated without ENP release high amount of nanoparticles (pieces of matrix paint). QUV ageing increase x2 the number of nanoparticles (not necessary engineered) released by comparison with an untreated paint. Increase of the binder amount and the quantity of the TiO2 pigment allow decrease ENP release toward zero. ***Protocol used for ENPs release into the water*** Painted panels were then exposed to accelerated artificial weathering test, i.e. standardized UV light exposure (EN ISO 10686) and abrasion (Taber test; EN ISO 7784-2), and finally immersed into water for different timeframe, according to EN ISO 2812-2:2007. These tests were applied to simulate aging and degradability of the paints in outdoor applications. Both painted panels (i.e. UV ray exposed and abraded panels, and un-weathered panels) were immersed in water in static conditions and with different frame-time, according to procedure described in ISO 2812-2:2007 opportunely adapted to our case studies. ENPs release from paints to water depends on: paint formulation: type and amount of ENPs, binder, pigments, etc.. Immersion cycles (wetting and drying cycles) of coated panels. While QUV aging and abrasion did not influence leaching of ENPs from coated panels. The results showed that TiO2 and Ag ENPs were not released from paint, while only a small release of Si was measured in leachates, with a maximum concentration of 108 mg/l after 120h of water immersion. The cumulative loss of Si from coated panel is about 0.7% with respect to initially amount of SiO2 applied. Microscopy investigation highlighted that SiO2 ENPs are mainly released in form of agglomerates, and that only very few single SiO2 ENPs were present. The results confirmed that release of ENPs from coating to water depends on paint ingredients, and migration is related to immersion cycles (wetting and drying cycles) of coated panels. UV ray exposure and abrasion didn't influence leaching of ENPs from coating. *Leaching test EN ISO 2812-2:2007 was selected and adapted to assess the ENPs release from facade paints in outdoor applications into water in normal conditions. Depending on the intended uses and application fields, different tests were identified. Accelerated weathering (UNI 10686 or UNI EN ISO 11507) tests to simulate degradability were applied. Coated panels were exposed to UV light in a QUV accelerated weathering machine for 500 hours according to ISO 11507. The QUV accelerated weathering machine reproduces the aging induced by sunlight, rain and dew on outdoor paints and coatings. It simulates in a few weeks, the aging that occurs over months or years outdoor. The ageing conditions (the applied irradiance cycles) were chosen to simulate natural weathering. For normal use, release of free or agglomerated ENPs is negligible.*

The task 2.2 was focused on the identification of the main entry routes in the environment and pathways for human exposure. Based on ENPs results release from paint during post-application of paint in dry and wet conditions we developed a conceptual exposure scenario for humans and workers for the three paint products studied in NanoHOUSE. We analyzed how ENPs may be released from paint during post-application of paint in dry and wet conditions, and shows how a conceptual exposure scenario may be derived for humans and workers for the three paint products studied in NanoHOUSE. From the results obtained, only a small release of SiO_2 ENPs was measured in dry and wet conditions. According to different products tested, it seems that there is a correlation between the release and the type of products. For all experiments, comparisons with the wet route and dry route results showed a correlation (i.e. the small SiO_2 ENPs release was observed for the C1 paint in both dry and wet conditions). The main human potential exposure routes are considered to be inhalation and dermal contact. Ingestion exposure is considered negligible although accidental exposure might occur through this route. The C1 paint removal or repair / demolition activities can lead to a potential SiO_2 ENPs release into air, affecting mainly workers but also humans via the environment through inhalation and dermal contact. Runoff from rain event can lead to a potential SiO_2 ENPs release into surface water, affecting mainly humans through dermal contact.

Task 2.3 was focused on selection and supplying of aged nanoparticles mixtures. Milling test was performed by using a Fritsch Mortar grinder, Mill pulverisette®, Type: 06002 866.Milling media, made of Zirconia, was conditioned by using 70% EtOH:water (v/v) solution (sterile water). Mass charge ratio (CR; i.e. ratio of grinding balls to powder) used for milling was 1:2 (i.e. 4 balls of 20 g and 160 g of powder), and different batch of milled paint was obtained. Grinding time adopted was 40 min, with a rotor speed of 320 rpm. Approx. 1 kg of milled paint for each sample (A1, A2, A3, C1 and C2) has been then sent to GFC for their UV exposure. CEA characterized all milled sample. Behaviour of milled products is different. Generally speaking, products were too plastic for reducing the size to a few micron level by Mortar grinder. In particular product B are made of big plastic particles/ pieces and it is very difficult to reduce their size by a simple grinding. Fritsch Mortar grinder, Mill pulverisette®, Type: 06002 – 866. Milling media, made of Zirconia, was conditioned by using 70% EtOH: water (v/v) solution (sterile water). Mass charge ratio (CR; i.e. ratio of grinding balls to powder) used for milling was 1:2 (i.e. 4 balls of 20 g and 160 g of powder), and different batch of milled paint was obtained. Grinding time adopted was 40 min, with a rotor speed of 320 rpm. All paints was remilled a second time at CEA. The material used was: PM 100 Planetary Ball Mil, Restch Grinding jar in α-Al2O3. α-Al_2O_3 balls 20 mm diameter for dry milling were used. A suitable homogeneous population of particles of size (distribution showing D(0,5) around 1µm) were obtained. Grinding on paint B was not sufficient in order to break up the pieces which are very elastic and hard to break therefore cryogenic grinding was performed.

3.3. WP03- Environmental fate

The development of new methods for detection, traceability and characterization of ENPs has been identified as a major achievement of the NanoHOUSE project. The development of synthesis processes for labeled TiO_2 and Ag NPs which could satisfy two conditions:

- To be as close as possible as pristine ENPs used in coatings regarding their surface properties, size and behavior.
- To be able to detect those NPs in complex environmental matrix (natural surface waters, soils, plants and biologic fluids).

The use of radioactive tracers for pristine ENPs is helpful as it allows more accurate detection limits than other analytical methods, to simplify the sample preparation, and to quantify the concentration profiles of deposited ENPs in a non destructive manner. But radioactive tracers cannot be used by all partners so an alternative ENPs synthesis based on fluorescent or metallic labeling had to be developed at the same time.

Synchrotron techniques are also particularly adapted to study the fate of ENPs in environmental systems because of their sensitivity, and of the possibility to combine imaging and speciation in unperturbed systems. Thus, it is possible to localize ENPs in soils, plant or animal tissues, and to track possible chemical transformations of ENPs, such as the release of ionic Ag from Ag NPs.

These labelled ENPs were used to study the transport of ENPs in soils columns. This study was focused on the effect of solution chemistry on the fate and transport of ENP in saturated porous media. First, we determined the stability of engineered nanoparticles suspensions under various solution chemistry conditions. Then, we examined the effect of solution chemistry on the retention and transport of engineered nanoparticles in saturated porous media. Silver (Ag) nanoparticles and Titanium dioxide (TiO_2) nanoparticles were chosen as examples of engineered nanoparticles.

The results obtained in this study show that a great majority of TiO_2 nanoparticles would transfer trough a soil. Therefore, the water table should be the environmental compartment with the highest exposition concerning TiO_2 nanoparticles. On the contrary, a great majority of Ag nanoparticles would be retained in soil. Therefore, the soil should be the environmental compartment with the highest exposition concerning Ag-NP nanoparticles.

The transfer of (i) pristine nanoparticles (nano-Ag and nano-TiO_2) and (ii) leachates from the paints A1 and B1 after ageing using the dry route (UV exposure and grinding) in crop plants was studied. Lettuce was chosen as a model, and both the foliar and root transfer were investigated, using a combination of physical, chemical and biological techniques. A transfer of pristine NP was observed both in the roots and leaves, but no phytotoxicity was observed. TiO_2 speciation was unchanged whereas Ag NPs were partly oxidized into ionic Ag. For the paint leachates, Ag was below the detection limit, whereas TiO_2 was transferred inside the roots and leaves. These results show that both the pristine NP and NP released from aged paints can be transferred into crop plants, and thus enter the food chain. Although no phytotoxicity was observed in our experimental conditions, further studies would be necessary to study possible effects at longer exposure times, and using finer toxicity markers.

With respect to the behavior of the released ENPs in natural waters, the most important factors for the assessment of the environmental fate of nanomaterials from paints were investigated:

1. Quantification of realistic release rates and the dependency on selected influencing factors (e.g. UV, influence of support material,…)
2. Identification of the released species/form (ionic /particulate, size)
3. Interaction with environmental compartments

The release of synthetic nano-TiO_2 and nano-SiO_2 from paints was size dependent investigated by artificial weathering from large panels in climate chambers. For the nano-TiO_2-containing paints additional leaching tests were also conducted on small panels. The results show that only very little release of nanoparticles occurs in these accelerated weathering studies. The concentration of release TiO_2 was only about 0.007% of the total TiO_2 in the paint. From the nano-SiO_2 containing paint mainly dissolved Si was released. Several experimental conditions (type of leaching medium, outdoor/indoor conditions, type of support, composition of paints, nature of UV exposure) were varied in order to study the critical parameters that could impact the quantity of TiO_2 particles released.

The further environmental fate of the TiO_2 released from aged paint in powder form was studied and compared to the pristine nano-TiO_2 particles. The stability of the nano-particles under varying physico-chemical conditions (pH, ionic strength, concentration of organic matter) were followed by bulk analysis, dynamic light scattering DLS and Zeta potential measurements. In addition natural water was also sampled from two different geographic areas and placed in contact with the synthetic nano-TiO_2. The results show that the released TiO_2 and pristine nano-TiO_2 behave very differently, especially in the presence of Ca where the released TiO_2 is much more stable than pristine nano-TiO_2, which is completely agglomerated at 3 mM Ca.

Overall the results from this task show that the paints chosen in the NanoHouse project release under natural weathering conditions only very small amounts of nanoparticulate materials. The released materials show a different environmental behavior compared to the pristine particles, which means that for assessing the environmental behavior and risks of released materials the pristine materials are not a good surrogate but that the actually released materials need to be studied.

At the end of the project the results from all tasks of WP3 and the LCA work from WP1 was combined in an exposure model. We performed a computer based modeling in order to derive predicted environmental concentrations (PEC) of nano-TiO_2 caused when this compound is applied in and produced for paint coatings. Knowing such PECs is crucial in order to estimate the environmental risks of engineered nanomaterials (ENM). Potential risks correlate with exposure concentrations and potentially negative effects for organisms at such concentrations. The exposure will highly be influenced by the nano-TiO_2 release potential of the target paints.

Unfortunately, environmental release rates and concentrations are not known too well and have only to a very limited extent been studied experimentally and analytically. Therefore, in this work, we developed release scenarios based on a stochastic (probabilistic) material flow model oriented towards a complete life cycle analysis of nano-TiO_2 produced and used in paint coatings. PECs in the form of probability distributions were computed for the surface water, soils (settlement area and sludge treated soils), and air compartments. Two scenarios (a low and high release scenario) were modeled. When taken together, those scenarios reflect so far the entire possible release (and environmental concentration) spectrum. Both scenarios are determined by inherent release volume uncertainties and in addition, are influenced by the distinct uncertainty related to the application and manufacturing quantities of nano-TiO_2. Additionally, a comparison of the paint-specific environmental concentrations to the ones of a comprehensive nano-TiO_2 model is presented. Such a comparison allows evaluating the environmental relevancy of the studied paint application when relating it to the total environmental significance of the complete nano-TiO_2 use.

The surface water concentrations for nano-TiO_2 from paints were for all scenarios at small ng/L levels. The annual increase of the concentrations in soils (in European settlement areas) were modeled at the most around 20 µg/kg (85 percentile) but most probably around or lower than 1 µg/kg. The results for sludge treated soil PECs are in the same µg/kg ranges. The air concentrations were at low ng/m^3

levels. The modeling results show that the contribution of facades to the total nano-TiO_2 flow to the environment are small.

Overall the work performed in WP3 shows that it is possible to study the behaviour and effects of aged and released ENPs in natural systems. Due to the low concentrations of ENPs in these released materials it is not always possible to detect the ENP in water or plant material and therefore the use of pristine materials is sometimes inevitable to get information on processes. However, a careful design of the experimental conditions allowed in most cases to investigate the fate in water and plant uptake under more realistic conditions than with the pristine ENPs. These studies with aged ENPs are among the very first studies performed with such real-world materials and the results are thus highly significant for risk assessors as they will allow to put the results from studies with pristine materials into a context where life-cycle emission of ENPs from actual applications are considered.

3.4. WP04- Hazard characterization

Summary description of the work performed; achievements

We researched the literature reporting biological effects of nanoparticle containing paints, prior starting the cytotoxicity studies. The findings of this research were summarized and published (Kaiser et al. Sci. Total Environ. 442 (2013) 282-289).

An endotoxin analysis of ENP and paints was not foreseen in this NanoHouse project.
However, an analysis of possible endotoxin contamination should be assessed prior evaluating the potential toxicity of a certain compound. In case of an effect it is absolutely essential to know, if the effect was initiated by an endotoxin contamination or by the sample itself. Our ENPs and paint samples were endotoxin free. KU Leuven tested at this occasion different endotoxin assays. The findings were summarized and published by Smulders et al. Part. Fibre Toxicol. (2012) 9:41.

In-vitro studies
The mechanisms of action of ENPs on the lung epithelium are not yet fully understood. It is shown that for some particles pulmonary responses have remote effects in e.g. the blood. Here we focused on inflammation in the lung and in the systemic circulation.
In vitro a multiple cell culture was used on a porous membrane: at one side pulmonary epithelium and macrophages on the other side endothelium. Here the *in vitro* cytotoxic effects of pristine NPs and paint particles on the status of the epithelial cellular monolayer were investigated.
The *in vitro* results show that the pristine TiO_2 and Ag ENPs show some cytotoxic effects at relative high dose, while pristine SiO_2 ENPs and all paints with ENPs and control paints do not. In the complex triculture model of the lung-blood barrier, no considerable changes were observed after exposure to the different pristine ENPs and paint particles.

ENPs might be released from painted surfaces during rain events and accumulate in the surface water and consumed by humans. Thus ingested ENPs will come in contact with cells of the gastro-intestinal tract and/or might affect our immune system. Thus cells of the gastrointestinal tract grown in the presence of nanoparticle containing paint particles behaved in comparison to cells grown in the presence of the corresponding paint particles without nanoparticles not significantly different. Thus nanoparticle containing paints should not lead to an additional uptake by cells of the gastrointestinal tract compared to paints without nanoparticles. Thus nanoparticle containing paints should not induce an additional health risk.

Similar results were obtained with immune cells. Immune cells grown in the presence of nanoparticle containing paint particles behaved in comparison to immune cells grown in the presence of the corresponding paint particles without nanoparticles not significantly different. Nanoparticle containing paints should not cause additional negative effects on our immune system, compared to paints without nanoparticles.

In our in-vitro studies it could be shown that the cytotoxic effect evolved by pure (pristine) nanoparticles is stronger than the effects evolved by the particles incorporated in a paint matrix. Nanosilver and especially ionic silver were the most cytotoxic substances among the three tested nanoparticles. Thus nanoparticles embedded in a paint matrix are less bioavailable and by that less toxic.

In vivo studies

To study the *in vivo* toxicity of pristine ENPs and paints containing ENPs, mice were exposed to the particles by oropharyngeal aspiration in a subacute protocol (5 exposures).

The *in vivo* experiments showed that the pristine ENPs have no effects on the blood parameters and a subtle toxic effect in the lungs, which was most pronounced in the case of the pristine Ag ENPs (increase in total cells and neutrophils, 2-fold increase in pro-inflammatory cytokines KC and IL-1ß). The paints containing ENPs did not show significant toxicity.

In conclusion, we demonstrated that although pristine ENPs show some toxic effects, no significant toxicological changes were observed when they were embedded in a complex paint matrix.

We evaluated the *in-vivo* effects of pristine ENPs and paint particles, applied topically on the skin, on the classical hypersensitivity reaction to a well-known potent dermal sensitizer (DNCB). In a previous study, we studied the effects of subcutaneously injected TiO_2 NPs on the dermal sensitization with DNCB.

The modulatory effects of different doses of TiO_2, Ag and SiO_2 ENPs and paint particles on the dermal sensitization with 0.1 % DNCB was investigated. In AOO-treated control mice, none of the topically applied pristine ENPs or paint particles significantly influence the stimulation index (SI). When pristine TiO_2 NPs were topically applied prior to DNCB sensitization, we found an increased SI value compared to vehicle applied DNCB treated mice. Pristine Ag and SiO_2 prior to DNCB sensitization did not significantly influence the SI. Application of the different paint particles did not influence the SI as well. In conclusion, we demonstrated that dermal applied pristine TiO_2 NPs act as an immune-stimulator on the dermal sensitization capacity of DNCB. In our previous study, similar results, but more pronounced, were found after subcutaneously injecting TiO_2 NPs.

Experimental evidence has been generated that NPs can migrate from the primary organs of intake, most often the lung, to secondary organs and tissues (e.g. heart, liver, kidneys) via the blood circulation.

In this study, we assessed the body distribution of different ENPs in mice in two sets of experiments: first particles were dosed in a multiple exposure regime (5 exposures during 1 month) finally the concentration of the particles in different organs is measured - only at the end of the experiment - by analysing the metal content via ICP-MS (this set of experiments is in this report named "**multiple dosing**") and a second set of experiments where particles after a single exposure were followed up to 3 months, here magnetic particles are measured *in vivo* via MRI in living animals at different timepoints and at the end of the observation period metal concentrations are measured as in the first experiment (this set of experiments is in this report named "**single dose**").

In conclusion, in the **multiple dosing** protocol only the pristine Ag ENPs show significant distribution to different organs (liver, spleen and kidney) only at the early time point, while TiO_2 ENPs did not. Concentrations of Ag and TiO_2 ENPs in the lung are higher at the early time point compared to the late time point 26 days later, indicating clearance of ENPs out of the lung over time. The paints containing TiO_2 (A1 and A2) show an increase in TiO_2 in the lung, but no distribution to other organs except to the liver (A1). Concerning the Ag containing paint (B1), the concentration of Ag in the paint is probably too low to be detected in lung and other organs. Due to a high background of SiO_2, no final conclusions could be drawn about body distribution of pristine ENPs and SiO_2 paints.

In the **single dose** protocol using core shell SiO_2-Fe_4O_3 ENPs, the ENPs accumulate in the liver after intravenous injection, while no significant distribution is seen after intratracheal instillation in the lung. No conclusions could be made about particle clearance in the lung, due to limitations of the used method (MRI).

Methodologies and approaches employed; main achievements compared to the state-of-the-art

At the start of the project, the reliability of 5 different assays to detect endotoxin (LAL assay and TLR4 reporter cells) were evaluated when performed in the presence of (nano)particles. Before this study, almost no research has been done to which extent nanoparticles can interfere with the different LAL assays. To our knowledge, only one (limited) study done by Dobrovolskaia et al. was published showing that endotoxin levels can be under- or overestimated due to the presence of nanoparticles (Dobrovolskaia et al. 2010).

To study the *in vitro* effects of pristine ENPs and paint particles, a complex triculture model of the lung-blood barrier consisting of human bronchial epithelial (16HBE14o-) cells, human monocytic cells (THP-1) and endothelial cells (HLMVEC) was used. In this model, recently developed at the KU Leuven, different parameters including barrier integrity, inflammation and oxidative stress can be investigated.

To study body distiribution, ICP-MS and magnetic resonance imaging (MRI) techniques were used. After exposure, different tissues (lung, liver, spleen, kidney and heart) were removed and particle (metal) content (TiO_2, Ag and SiO_2) was determined using ICP-MS.
In another experiment, specific core shell nanoparticles consisting of a shell of SiO_2 and a magnetic core of Fe_3O_4 were developed at CEA, which allow us to detect these particles using micro MRI (Bruker Biospec 9,4T) to study body distribution over a longer time period

New experimental protocols were developed to study the immunomodulatory effects of particles on the dermal sensitization process of DNCB. To this end, a known test model to detect chemicals with a sensitization potential, the mouse Local Lymph Node Assay (LLNA), was adapted to study the effects of particles. In the adapted protocol, particles were injected subcutaneously at the dorsum of both ears 1 hour before the first sensitization. In a second experiment, particles were suspended in a 1.6% hydroxyethyl cellulose (HEC) gel and applied topically in the area around/between the ears 1 day before the first sensitization.

We investigated the modulation of airway hyperreactivity and inflammatory response by pristine ENPs and paint particles in a mouse model of diisocyanate-induced asthma. This mouse model was developed and validated at the KU Leuven (Vanoirbeek et al. 2004, Vanoirbeek et al. 2008, De Vooght et al. 2012)

We were able to show that paint particles containing nanoparticles do not affect cell morphology (bright field microscopy), cellular up take (transmission electron microscopy), release of reactive oxygen species (2',7'- dichlorodihydrofluorescein-diactate test), cytokines (Elisa), cell activity (MTS conversion) and cell death (apoptosis/necrosis by flow cytometric analysis, FACS) in a different manner than the same paint particles without nanoparticles. The obtained data concerning effects of ENPs and paint particles was conducted with cell cultures with a high number of living cells. All test procedures used in this study were reliable and suitable for the in-vitro cytotoxicity testing of ENPs and paint particles up to concentrations of 243 µg/ml.

Our in-vitro studies with cells of the gastrointestinal tract and cells of the immune system are in accordance with the studies of other researchers, who investigated the effects of paint dust in in-vivo and in in-vitro systems (Saber et al. 2012a, Saber et al. 2012b, Mikkelsen et al.2013). These scientist could demonstrate that oxidative stress, inflammation or DNA damage were independent from the presence of nanoparticles in the paint. Similar findings were reported from amorphous silica dioxide. In several inhalation studies with respirable amorphous silica dioxide particles it were demonstrated that the particles produced a time- and dose-related local inflammation response of the animals lung tissues. However, this response was transient and reversible after termination of exposure (Arts et al. 2007, Merget et al. 2002). Koponen et al. 2011 could demonstrate that the incorporation of nanoparticles into paints won't lead to a severe increase of nanosized particles in the environment (Koponen et al. 2011). It can be assumed that released nanotitanium dioxide particles will agglomerate and adsorb to other particles and by that these particles won't persist in the water column. They will be transferred into the sediments, where they are less bioavailable and by that won't lead to an accumulation in the foot chain. The early results of our in-vitro and in-vivo studies and the results from the in-vivo studies suggest that the use of engineered nanoparticles in paints should not result in an increased exposure level of nanosized materials and should not increase a nano-related health risk to users compared to the conventional paints without engineered nanoparticles.

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3.5. WP05- Safer use and waste management

The main objectives initially planned in WP5 were: to quantify the potential release of ENPs from end of life of paint, to explore possible final treatment solution of ENPs containing waste, and finally to improve the safety of studied paint. In order to reach these objectives, the WP5 was structured in different tasks described as follow.

Initially, we performed a detailed state of the art (task 5.1) concerning the end of life of nano-based products, focussing on nano-based paint and coating. The emphasis was on identifying suitable policies, guidelines, standard and approaches applied to nanowaste management, as well as on methods and analytical techniques used to investigate the end of life of paints studied in project. The results were reported in D5.1. This also allows to set up the different experiments performed in task 5.2 of WP5. Taking into account that we still have very limited information concerning end of life of nano-based product, and the fate of the different ENPs when nano-based products are discharged has not been yet investigated, we proposed and shared with all NanoHOUSE partners some experimental protocols to investigate the landfill behaviour and incineration of ENPs- containing paint debris. In detail:

- The release of TiO_2, Ag and SiO_2 ENPs from paint debris (i.e. powders like fine grains) was investigated by an appropriate leaching test in task 5.2, in order to simulate a possible disposal in landfill of that debris resulting from abatement, renovation, or demolition activities. The EN ISO 12457-3:2002 standard was applied by using two different liquid to solid ratio (L/S), i.e. L/S=2 and L/S=8. The results show that only very little release of SiO_2 and TiO_2 ENPs occurs in these leaching studies. The release of TiO_2 was quantified only about 0.0001% of the total TiO_2 in the paint, while the release of SiO_2 ENPs was measured about 0.05% (w/w).
- The TiO_2 ENPs found in leaching liquids seem to be attached to other organic materials, probably organic binder leached from the paint. Electron microscope images showed that single SiO_2 ENPs were released mostly as aggregated particles, due to likely binder used in paint. Other paint constituents were released during leaching test, as other inorganic particulates materials.
- The leachates obtained from the leaching test with paint debris were also used to test the ENPs diffusion through a geomembrane (i.e. thin polymeric membrane used in landfill site). The membrane efficiency to TiO_2 and SiO_2 ENPs diffusion after 80 days of aging was demonstrated.

The efficiency of geomembrane was also demonstrated after 100 days of aging, even if damages of polymeric membrane (brittleness, cracks) were observed.

- SiO_2 and TiO_2 ENPs used into the paints didn't cross the membrane after over one month of constant exposure, which corresponds to an effective efficiency of the geomembranes used in landfill over 12 years in real conditions.
- The thermal behaviour of TiO_2, SiO_2 and Ag ENPs in paint debris was investigated by lab thermal treatment test (incineration) in electric furnace. The results show that TiO_2, SiO_2 and Ag ENPs are not emitted with flue gas in these incineration studies. Only micron-sized particles (inhalable dust) mainly constituted of CaO were released during these test.
- The incineration of paint debris produced dust, but we didn't observe an increase of dust concentrations in comparison to paint debris without ENPs.
- The majority of Ti, Si and Ag was found in the solid combustion residues, i.e. ashes, resulting from incineration. The concentration in ash of Ti, Ag and Si was 35%, 0.004% and 15.7%, respectively. Taking into account that the total weight loss of paint debris sample after thermal treatment ranged from 39.5 wt. % to 53.4 wt.%, the measured amount of Ti, Si and Ag in ashes fit well with the initial amount of that elements in paint. SEM-EDX analysis showed that TiO_2 and SiO_2 remained on the surface of the ashes, even if we were not able to verify if it remained as ENPs.
- Weight losses of paint debris which occur in temperature range 220–380℃ and 400–460℃ are due to emission of organic compounds included in paint formulation (e.g. binder). Weight loss which occurs in temperature range 620–780℃ is due to decomposition of the carbonaceous matter present in paints. CaO is the most abundant compound that we found in all ashes, which constitutes up to 82 wt. %.
- With regard to potential end of life solution, the ashes resulting from thermal treatment of paint debris were vitrified with suitable additives (i.e. glass cullet and feldspatic inert). Glasses obtained are mainly constituted of CaO and SiO_2. TiO_2 is also a major oxide in glass resulting from vitrification of ashes from A1 sample, as expected. During melting, SiO_2 as the main components of vitrificable batch formed a glassy structured matrix.
- Water leaching test were also conducted on the obtained glass following the methods of the EN ISO 12457-2:2002 standard. The analysis of leachates showed that that both Ti and Si are strongly immobilized in glassy matrix, as the amount of Ti and Si in leachates were below the detection limit. As the amount of Ag in ashes, and in glass, was very low, we didn't expect to find Ag in leaching liquid.
- The vitrification previously applied in the immobilization of urban and industrial waste streams, may be then considered as potential safer option for the treatment of solid nanowastes.
- With regard to design of safer paint, we formulated new SiO_2 ENPs containing paint, by changing the nature of the binder (organic versus inorganic), the pigment volume concentration (PVC), the particle size of the binder, and the surface morphology of pigments. These new paint were assessed by means leaching and abrasion test to quantify Si release.
- In general, a lower leached amount of Si was measured for new paint formulation, in comparison to initial tested paint, during the leaching test. Also, the TEM analysis showed that very few single Si ENPs are released from new paint formulation, while much more SiO_2 ENPs were released from initial C1 paint.
- During the abrasion test of new paints, we measured a lower number of nanosized particles released (not necessary engineered) in comparison to initial paint tested, especially with regard to paint with higher amount of binder. Free or agglomerated SiO_2 ENPs were not observed in any case.
- For paint exposed to UV light (QUV test), we observed during the abrasion a higher release of nanoparticles for paint sample with new binder, and agglomerates of SiO_2 ENPs were observed. While, for paint sample with new PVC, we noted a lower release of nano-sized particles. According to results of both leaching and abrasion test, by changing the PVC in new paint formulation, it is possible to reduce the release of free and agglomerates of SiO_2 ENPs, while the nature and amount of micronsized pigment (i.e. TiO_2) may be a solution to decrease strongly ENP release for paint exposed to UV light.

Methodologies and approaches employed and the achievements of the project compared to the state-of-the-art.

At the time when NanoHOUSE was conceived it was stated that there were not available data and information on management of nanowaste, especially with regard to the fate of different ENPs when nano-based products are discharged. Also, it was not known how much ENPs are contained in waste stream. An approach proposed at that time was to take the complete life cycle of nano-based products into consideration when assessing the risks of ENPs. In NanoHOUSE a systematic investigation of the ENPs-containing paints life cycle stages (i.e. production, use, end of life) was performed to provide an holistic perspective on risks and on opportunities of that product. In this WP, we posed our attention on end of life of ENPs-containing paint. At the end of the NanoHOUSE project, we can conclude that the release of SiO_2 and TiO_2 ENPs from solid paint debris is insignificant with respect to the initial amount of ENPs in paint (amount released is << 0.1%). We studied paint debris, as these residues resulting from paint removing and recoating of the exterior surfaces of houses; these activities are periodically required during the operating lifetime of the home building. In addition, the disposal of construction material coated with ENPs- containing paint are often crushed in debris for further re-use in construction stream. Although there are a variety of test procedure available to characterize waste with regard to their landfill behavior (equilibrium or semi-equilibrium leaching test, dynamic or static, pH static test, etc.), our results highlighted how liquid to solid ratio is a physical factor strongly affects the release of ENPs from granular solid waste. Also, we observed that the release of ENPs is due to diffusion of paint constituents with leachant flows (i.e. water), i.e. the leachant flow around the solid paint debris during dynamic leaching scenario is able to dissolve paint.

With regard to waste treatment technologies, it is well known that a long-term integrity and durability of geomembrane lining systems is required as barriers between potential contaminants and groundwater in landfills. In the case of municipal solid waste landfills, the chemical dissolution and degradation of the typical high density polyethylene (HDPE) geomembrane is considered to be a non-issue. However, the impermeability of HDPE geomembrane to ENPs-containing leachates has never been investigated. In NanoHOUSE we firstly demonstrated that HDPE geomembrane are effective as barrier to SiO_2 and TiO_2 ENPs containing leachates.

Then we focused our attention on incineration processes, as more than 100 million tons of municipal solid waste are incinerated every year in EU, Today, little is known about the fate of ENPs during incineration, and we cannot exclude that ENPs containing paint waste may enter in incineration plant. First literature data showed that inorganic ENPs (i.e. CeO_2) were not released into the atmosphere during incineration of ENPs containing waste in a incineration plant, but were found in combustion residues, i.e. ashes and slag (Walser et al., 2012. Nature Nanotechnology 7: 520-524). As combustion residues are usually disposed in landfill, there is a clear need to develop method to avoid release on ENPs from these residues. Evaluation of risks related to waste incineration of polymer nanocomposites based on a desktop study without accompanying experiments has been recently performed (Roes et al., 2012. Science of the Total Environment 417–418: 76–86). In any case, further research is required to reveal which nanomaterials will actually be emitted to the environment following incineration of nanowaste. In NanoHOUSE, we confirmed that ENPs used products (i.e. paints) were not emitted with fumes during lab scale incineration test, but were attached to the surface of the ashes. In addition, we demonstrated that ENPs containing ashes may be vitrified, by adding glass-forming additives resulting from material recovery (i.e. glass cullet and feldspathic inert). Obtained glasses were also stable to water leaching. Then, the WP5 significantly extends the current state-of-the-art in the fate of ENPs during end of life of nano-based product, by developing and implementing reliable integrated experiments at lab scale and for different type of ENPs-containing paints. These test were applied to measure directly the release of ENPs by employing different analytical technique and methods.

Engineering nano-based product with reduced ENPs release that maintain valuable functional properties is crucial to the sustainability of the nanotech industry. In WP5, a safer formulation concept for nano-based paint was demonstrated. It is based on the PVC parameter, i.e. nature and amount of binder and pigment in paint. Our results showed that the proposed method can be used to effectively reduce the release of SiO_2 ENPs from paint. Although other factors such as overall paint composition and complex ageing processes of paint in the environment (e.g. UV exposure) could influence the release, this scalable method can be applied in manufacturing of paint developing safer by design nano-based paints.

3.6. WP06- Project dissemination, ethics and nanorisks issues

The introduction of ENPs in commercial products is viewed with apprehension by the public at large. This can clearly slow down the progress expected to be obtained with nanomaterials by an excessive prudence of the European industrials. The case of ENPs used in building construction materials is of course of main importance for the public as we mainly spend our time in houses and offices, etc. In addition, building industry is becoming one of the largest users of inorganic ENPs (e.g. TiO2 and SiO2). A large dissemination of the information regarding nanosafety results could positively contribute to reassure people. In this context, the EU- funded NanoHouse project addresses this societal challenge in order to relativize the fashionable doom-watch imagining nanoparticles invading massively our environment; and make industrials aware of their products in terms of potential Health and Environmental impacts.

Started in January 2010, FP7 NanoHouse project brings together scientists and paints manufacturers partners and contributed to the development of appropriate solutions for the use of safe, sustainable and competitive nano-based paints – ENPs containing paints - through their whole life cycle (from cradle to grave). To that end, four main strategic issues were developed:

1. Life Cycle Thinking applied to TiO2, Ag and SiO2 ENPs containing paint, by identifying data gaps and lacks of knowledge considering Environmental Health & Safety issues,
2. Identification of ENPs sources and quantification of the released ENPs during the use phase, post application/service life and final disposal of nano-based paint,
3. Evaluation of the environmental and the toxicological behavior/effects of the released ENPs from 'aged nano-based paints by comparison with the pristine ENPs (i.e. as received and added in paint),
4. Development of new safer solutions for nanowaste management, coming from the end of life of nano-based paints,
5. Reduction of the release-ability of nanoparticles from paints by proposing safe-by-design solutions of the nanoproducts (paints or coating).

On each of these strategic issues, a rationale understanding argumentation is developed in order to clarify the potential risk and the sustainability relative to nano-based paints. Dissemination reports, posters and quiz were produced and largely used during EuroNanoForum. All these documentation is available on NanoHouse website.

4. DESCRIPTION OF THE POTENTIAL IMPACT

4.1. WP01- Life Cycle Thinking

The combination of LCT and Risk Assessment (RA) enables a holistic and systematic analysis of the potential benefits and risks of ENP enhanced façade coatings.

The results of NanoHouse are supporting the decision making and may provide improvement opportunities for:

- safe product design
- functionalities
- production processes
- disposal/recovery/recycling methods

To avoid misdirected investments (i.e. not competitive products), risks to the environment and health, see the following recommendations:

a. Evaluation of potential benefits during early stages of innovation.
b. Explore potentials for the improvement of environmental performance.
c. Testing the product to compare functional improvement to conventional product.
d. Safe design:
  - Select ENP depending on the product related exposure scenarios and the state of knowledge on ENP specific hazards
  - Bonding of ENP in the coating matrix is relevant in order to avoid unintended release during the use phase of façade coatings
e. Occupational health: Obtain and use the ENP in their gel, fluid or paste-like formulation, avoid airborne ENP, avoid ENP containing dust during maintenance or recycling phase, e.g. of building waste.

f. Waste and leftovers: Clarify if industrial residues are properly disposed and that established recycling systems (i.e. containers, road making) will not be disturbed due to ENP inclusion in the stream.
g. Industrial waste water should be pre-treated and clarify if ENP are eliminated by waste water treatment facilities.

Applying LCT provides to a win-win situation: helps to identify opportunities and leads to decisions, which may improve environmental, safety and functional performance.

4.2. WP02- Sources identification

In terms of environmental impact, it is essential to identify the emission sources, and then in case of release, to evaluate the fate of released nanomaterials in environmental compartments (air, aquatic systems, and soils), possible chemical transformations and transfer and impact to living organisms. Solutions to detect nanoparticles into the environment were developed at short term. Solutions for the end of life treatment of the paints: incineration, disposal into the landfill were developed as well.

In terms of economic impact, ENP source emissions understanding from nano products in general should be one of the success conditions for a ‘Nano Responsible Label’ definition. This Label could guarantee a Safe by Design process in order to respect Human Health and Environment during all Life cycle of the product. The availability of international standards for coatings is numerous. However there are not e.g. ISO standard specifically devoted to paint containing nanosized fillers. Accordingly we used existing standards opportunely adapted to our case study. There is a need for standardization of coating preparation methods, leaching protocols for assessing nanosized fillers migration, and also for characterization activities / analysis of ENPs in products (e.g. coatings) and other matrix as water. According to the paints manufacturers, there is an urgent need to develop new specific standard for nanoparticles containing products. In particular, standard methods for the characterization of nanoparticle release are currently not available. **This issue is of prime importance to speed up the commercialization of nanoproducts** as if ones can prove that no nanomaterial is released during usage and end of life of the product. Exposure is limited and the consecutive risk could be maintained acceptable whatever the biological response of the nanomaterial. The experimental work performed on the quantification of the released sources of ENPs allowed to develop experimental protocols able to assess nanoparticles release that could be recommended as standards.Nanohouse project used different existing standards opportunely adapted to paint containing nanoparticles case study: Taber (Taber test; EN ISO 7784-2) widely used in industrial applications to simulate wear of the coatings was adapted with the appropriate metrology of the nanoparticles in order to assess the potential nanoparticles release induced by abrasion into the air. Taber method using harsh abrasion (SiC paper) allows assessing the ability of nanopaint to release nanoparticles into the air with a high sensitivity. EN ISO 2812-2:2007: leaching protocol was adapted in order to assess the potential nanoparticles release from facade paints in outdoor applications into water in normal conditions. EN ISO 12457-3:2002: Appropriate instruments able to assess the potential nanoparticles release into liquids were chosen in order to characterize the paint debris in granular form (i.e. powder) disposed of in a landfill in leaching conditions. Depending on the intended use and application field, different tests were identified. Accelerated weathering (EN ISO 10686) and abrasion (Taber test; EN ISO 7784-2) to simulate degradability were applied. Source emission is a key point of the ENPs release issue for the market and the social acceptance of nanoproducts. These techniques allow to assess the ability of a paint to containing nano to release nanoparticles.

In terms of social impact, ENP source emissions pragmatic identification is necessary in order to: relativise the fashionable doom-watch imagining nanoparticles invading massively our environment and make industrials aware of their products in terms of potential Health and Environmental impacts. The introduction of nanoparticles in commercial products is viewed with apprehension by the public at large. This can clearly slow down the progress expected to be obtained with nanomaterials by an excessive prudence of the European industrials. The case of nanoparticles used in building construction materials is of course of main importance for the public as we mainly spend our time in houses and offices, etc. A large dissemination of the information regarding nanosafety results can positively contribute to reassure people. WP2 results at the end of the project were summarized in 4-

pages reader friendly Dissemination Reports (DR 2) and put on the Nanohouse Website. Nanohouse public website has been created in order to support communication and technical document transfer. NanoSmile web site dedicated to communication on Nanosafety issues, lunched in the frame of the ended NanoSafe2 project is continued through NanoHouse project.

4.3. WP03- Environmental fate

Release of engineered nanoparticles (ENP), from façade coatings on buildings may result in transfer to the environment. Due to the lack of data on the behaviour of the released ENP under natural conditions, it is essential to study their release and fate to enable a better assessment of the risks of ENP for environment and human health. Studying the mechanisms of release and environmental fate of ENP is essential for better assessing their risks for the environment and human health.
The behaviour and the effects of pristine ENPs have been investigated by many projects in great detail. The work performed in WP3 of NanoHouse has shown that it is also possible to design experimental procedures that allow to investigate the fate and effects of aged and released materials. There is currently a lot of interest on a conceptual level on the emissions of ENPs and the aging processes. In this situation NanoHouse is able to provide some first results and is thus able to establish itself as a project at the forefront of the discussion on the risks of real nano-applications. The great advantage of NanoHouse was release from a relevant application was investigated, an application that is gaining more and more attention by regulators and the public. Due to this unique position of the project, the results from WP3 will make a long-lasting impact. They will directly feed into the next round of FP7 projects, mainly NanoMILE, where B. Nowack is leader of the WP on “Life cycle evolution of nanomaterials” and SUN, where B. Nowack is leader of the WP on “Environmental fate, release and exposure”. These two projects will extend the release and fate studies of released particles to more particle types and other applications. Some partners of NanoHouse are also involved in these projects (e.g. CEA in NanoMILE), so the results will definitely feed into the scientific community and be used by other researchers. Both projects will have a much larger emphasis on risk assessment, so the importance of aging and release that was tackled for the first time in NanoHouse will continue to be fed into the risk assessment process for ENPs.

4.4. WP04- Hazard characterization

Socio-economic impact
Paints with ENPs shouldn’t cause additional health effects, compared to paints without ENPs. Thus the paint industry has now the possibility to manufacture a new generation of paints with ENPs that possess excellent, improved properties, such as water repellence, scratch resistance, improved durability and antibacterial properties. The painted surfaces will be longer and better protected against chemical and physical weathering and against biological degradation.

ENP doped paints with improved properties compared to conventional paints without ENPs would have a huge socio-economic impact. The painted surfaces would be longer protected. Refreshing of painted surfaces would have to occur not as often as with conventional paints. This will save work power and money. At this occasion we want to point out that the price of a product has a significant impact on the consumer acceptance. Thus the paint industry must find a way to improve the properties of the paints without significantly increasing the price for their products.

Societal implications
The toxic effects of ENP-containing paints were similar to the observations made with conventional paints without ENPs. According the preliminary results it can be assumed that ENPs-containing paints did not possess a higher health risk compared to conventional paints without nanoparticles. This is true for the tested ENPs (nanosilver, nanotitanium dioxide, nanosilica dioxide).

The release of single ENPs from paints was far lower than the release of microparticles or ENPs embedded in paint matrices. The released not embedded ENPs will certainly bind to other particles and will form larger aggregates, which are less bioavailable and by that shouldn’t lead to an accumulation in the foot chain. We don’t assume that free ENPs will accumulate in the environment.

The production of ENPs-containing paints should not result in an increased exposure level of nanosized materials.

Activities and exploitation of results
The paint industry will have to prove that the ENPs in paints are achieving the proposed benefits. There are currently no long term studies available. Therefore the paint industry will have to prove that they were able to produce ENPs doped paints with improved properties. These improvements should be sustainable and last for a prolonged time period.

The preliminary results, which are nowadays available, suggest that the use of ENPs containing paints should not cause an additional health risk to consumers. However a creeping immission into the environment is not excluded and the consequences were not fully assessed yet. From our in-vitro and in-vivo results we can assume that ENP doped paints wouldn't cause acute health effects. Nevertheless a surveillance of a possible ENP accumulation in the environment over the years and possible adverse effects after a prolonged time period is absolutely necessary.

4.5. WP05- Safer use and waste management

The WP5 contributed to the strategic goal of promoting sustainable management of the solid paint waste containing ENPs by advancing our knowledge on the end of life / treatment solutions of that waste, and on safer-by-design approaches to reduce the release of ENPs from paint's life cycle phase. Management of solid nanowaste could constitute an important source of ENPs release into the environment. Research within the WP5 has led to improved knowledge on potential release of ENPs coming from management of ENPs containing waste. WP5 placed particular emphasis on the interactions between paint waste management and environmental impacts resulting from treatment options of that waste. This has led to an integrated test, methodologies and approaches needed to assess these impacts. In particular, WP5 has achieved significant scientific innovations, including: (i) solid nanowaste treatment strategies, through a quantitative assessment of concentration of ENPs released from nano-based paints' end-of-life, the identification of waste stream which merit immediate attention, i.e. paint debris, ashes, etc., and the application of suitable inertization process to combustion residues containing ENPs; (ii) improved current emission estimates for anthropogenic sources of ENPs, providing guidance in the selection of relevant standard methods to simulate end of life scenarios, as well as how to adapt these methods for the evaluation of ENPs release; (iii) application of safer-by-design approach aimed at reduction of ENPs release from paint, by changing relevant paint formulation parameters affecting paint features;
The results of WP5 will have an impact on policies relating to the management of nanowaste, and impact on paint industry with regard to development of suitable guidelines / procedure for a safer management of paint waste. Preliminary studies on nanowaste do not sufficiently take into consideration the potential waste treatment solution. The technologies that can adequately treat, clean up, and dispose nanowastes still remain underdeveloped or are at the infancy phase of research and development. The WP5 presented a unique approach to address these issues, as this WP strived for an integration of methodologies and approaches, supported by analytical techniques, needed to investigate release of ENPs from management of solid paint waste, but also to assess suitable treatment process for specific waste stream containing ENPs (ashes). The results of the WP5 will contribute to an increasing awareness of problems existing in nanowaste management. In addition, research and development activities carried out in WP5 will allows in future to set up standardized test for certain possibly relevant release mechanisms, and to derive quantitative information of possible release rates.

4.6. WP06- Project dissemination, ethics and nanorisks issues

To develop nanotechnology we need an atmosphere of confidence. No trust no market! In this context this project brings together scientists and paints manufacturers partners and contributes to clarify to the public the potential risks of using engineered nanoparticles in facade coatings.

Focusing on innovation societal issues like life cycle thinking, nanoparticles release, potential toxicity of the aged paint containing nanoparticles, nanowaste management and safer design recommendations for paint manufacturers, NanoHouse potential impact could be summarize in 5 points:

1) During use phase, the nanoparticles seem to be stably attached to the coating, but the production and recycling phases could be hot spots for unintended release.
2) For normal use, release of free or agglomerated nanoparticles is negligible. Under hard abrasion and leaching tests, nanoparticles are mainly released embedded into the matrix paint or in form of agglomerates.
3) Using both in vitro and in vivo methods, the potential toxic effect of pristine engineered nanoparticles and aged paints containing nanoparticles were compared. The pristine nanoparticles examined in this project showed some toxicity at elevated concentrations. After aging, paints containing these nanoparticles show no significant toxicological changes compared with pristine nanoparticles.
4) Simulation of landfill conditions showed insignificant release of nanoparticles, geomembranes are able to block potential release and there is no evidence of nanoparticles emitted with fumes during incineration experiment.
5) Finally, testing different paint formulations for safer design shows that it is possible to reduce the nanoparticles release during the abrasion and leaching tests by adjusting the properties of the binder in combination with common pigment

5. NANOHOUSE CONSORTIUM

Beneficiary Number*	Beneficiary name	Beneficiary short name
1	CEA	CEA
2	Eidgenössische Materialprüfungs- und Forschungsanstalt	EMPA
3	Consorzio Venezia Ricerche	CVR
4	Katholieke Universiteit Leuven	KULeuven
5	Université Joseph Fourier - Laboratoire de Géophysique Interne et Tectonophysique	UJF-LGIT
6	MATERIS PAINTS ITALIA	MATERIS
7	GFC CHIMICA	GFC
8	AKZO NOBEL COATINGS S.A.	AKZO
9	PPG AC France	PPG

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