Life Cycle Considerations For Engineered Nanomaterials: A Case Study For Nano-Enabled Coatings On Drywall

C.M. Sayes and G.D. Rothrock

Center for Aerosols & Nanomaterials Engineering, RTI International, RTP, NC, USA, 27709, csayes@rti.org and grothrock@rti.org

ABSTRACT

Engineered nanomaterials are being incorporated at an increasing rate into various elements of the building industry. Nanoparticles have unique properties and offer tailored benefits to the traditional functions of building materials. Nanoparticle composite coatings are opening up new market opportunities in the global coatings arena, offering properties such as anti-microbialism, thermal insulation, dirt and water repellency, hardness, corrosion resistance, flame retardancy, UV stability, anti-graffiti, self-cleaning, moisture absorbing, and gloss retention. Global revenues for nanocoatings in 2011 were estimated to be $1.6 billion [1] . Particles engineered at the nanometer size scale have been demonstrated as replacements for toxic biocides in applications including air purification, thermal insulation, and self-cleaning. The utilization of engineered nanomaterials in the building envelope is expected to develop rapidly; however, the safety of these novel materials to humans and the surrounding environment must be studied in parallel to their incorporation into consumer products. Currently, there is much uncertainty in the risk of using these materials in the building industry. One valuable way to gather information critical to the development of safe nanomaterials is using a product life cycle approach that integrates product development with manufacturing and worker/consumer exposure. This specific research approach investigates a white paint product as a case study. The bulk material (i.e. dry wall) is characterized with the nanoparticle-enabled product (i.e. white paint) in its intact and degraded forms. Simulated wear-and-tear scenarios are performed on the painted wall, and the released aerosolized particles are analyzed for concentration, size, and composition. Lastly, the released particles are collected and exposed to pulmonary tissue for a toxicological evaluation. Results show that differential physicochemical properties and toxicological responses are induced between particle-types that contain engineered nanomaterials versus particle-types without incorporated nanomaterials. The impact of this research will help to enable sustainable opportunities of nanotechnology in the built environment, and provide methodologies for understanding nanomaterial properties in the context of a developed consumer product.

Keywords: nanomaterials, building materials, titanium dioxide, life cycle analyses, characterization

1 INTRODUCTION

Nanotechnology can bring great advantages to the building industry for sustainable development through the use of engineered nanomaterials in commercial grade products. For example, nanoparticles can increase the resistance to aging (UV, mechanical stress, etc.) of construction materials, particularly paints and coatings; they can replace toxic organic biocides, and thus be advantageously used for air purification, thermal insulation, and self cleaning, to name a few. Nevertheless, the development of nanomaterials in this economic area can develop dynamically only if the safety of humans and the environment is satisfactorily resolved. As far as human exposure is concerned, addressing the issue of safety, and consequently of acceptability of nano-enabled products calls for a focus on the places where people live and work. The purpose of this research is to gain knowledge into the life cycle assessment of engineered nanomaterials in common paints and coatings. This is accomplished using a product life cycle approach.

A product life cycle approach integrates product development with manufacturing and consumer and occupational exposure, enabling an opportunity to elucidate the human and environmental impacts of a technology. In life cycle approach for engineered nanomaterials incorporated into paints and coatings for use in residential homes has four main stages where exposure might occur. These four main stages are: (1) raw material production, (2) product manufacturing, (3) consumer use scenarios, and (4) product end of life disposal. The two main exposure endpoints are either environmental release or hazard to humans. In the environmental exposure scenarios, release of pristine particles or formulated composites as industrial air emissions, industrial wastewater processes, or trash produced by consumers of formulated composites are the major sources of concern. In the human exposure scenarios, release from "worn-and-torn" formulated composites (as in the case of weathered products, or do-it-yourself projects with older homes) into aerosolized particulate matter in the air or solid particulates that deposit on surfaces are the major sources of concern. Further identification of potential hazards from these sources require toxicity testing using appropriate model test systems depedning on the type of exposure, i.e. lung tissue for

inhalation, skin tissue for dermal, and gastro-intestinal tract for ingestion.

2 MATERIALS AND METHODS

The following methodology was developed to characterize the product life cycle of titanium dioxide (TiO2) nanoparticles incorproated into latex-based paint and subsequently coated onto drywall. Using this test material, there are three main phases in which the nanoparticle-enabled product could be used in residential homes or commercial building and where exposure to humans (workers or consumers) might occur. These phases include: (1) raw material production, (2) product formulation, (3) product installation, and (4) product wear-and tear. A fifth phase may include product end of life waste disposal; however, this research does not include this stage of life cycle.

The exposure to humans requires endpoint testing. In these exposures, release of "worn-and-torn" formulated composites into aerosolized particulate matter in the air is a major source of concern. Identification of potential hazards from these sources requires toxicity testing using pulmonary model test systems.

2.1 Characterization of Unformulated TiO_2 Nanoparticles

Three different TiO_2 nanoparticels (Tronox CR-826, Tronox CR-828 and Tiona-596) were used in this study. Several material characterization techniques were employed to thoroughly characterize the pristine TiO_2 powders. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy reveal critical information about the particle size, shape, aggregation states and morphology. Fourier Transform Infrared Spectroscopy (FTIR) was employed to analyze chemical composition of samples. Finally, X-ray diffraction (XRD) analysis confirmed crystal structure. Figure 1 shows the electron micrographs of the three pristine TiO_2 nanoparticles.

2.2 Formulation and Characterization of Formulated TiO_2-Enabled Paint on Drywall

The paint formulation includes the base paint (with and without TiO_2) mixed using commercial specifications. It is then poured into a slot coater and drawn to achieve uniform paint thickness on the dry walls. Finally, the coated surface is allowed to dry completely. Figure 2 shows pictures of the steps in this process.

2.3 Wear-and-Tear Methods for Formulated TiO_2-Enabled Paint on Drywall

The surface of the formulated TiO_2-enabled paint on the drywall is abraded by attaching a jumbo collet to a Taber Abraser 5900 Reciprocating machine [2, 3]. Powders from each sample are collected in vials analyzed using TEM, SEM, FTIR and XRD. Figure 3 shows the pictures of the steps in this process. Figure 4 shows the electron micrographs of the powders abraded from the formulated TiO_2-enabled paint on drywall.

2.4 Cytotoxicity Testing of Unformulated TiO_2 Nanoparticles and Formulated TiO_2-Enabled Paints on Drywall Powders

Two cell lines were used in this study [4, 5]. The initial cytotoxicity screen was probed using HDF (ATCC, Manassas, VA) cultured in Dulbecco's Modification of Eagle's Media supplemented with 10% fetal bovine serum and 1% l-glutamine, penicillin, and streptomycin. Studies were expanded to include immortalized human lung epithelial cells to monitor the production of inflammation mediators. Human lung epithelial cells (A549) (ATCC, Manassas, VA) were cultured in F-12K media supplemented with 10% fetal bovine serum and 1% l-glutamine, penicillin, and streptomycin. For both cell lines, passage numbers 2–10 were used in the experiments, and cells were seeded at a minimum density of 2.5×10^5 cells/mL. For these experiments, cells were exposed to uncontrolled ambient light conditions either with or without TiO_2 powders ranging from 0.001 to 10 ppm dosing concentrations.

Various biochemical endpoints were examined in this report. For these analyses, all chemicals were purchased from Invitrogen at the highest purity unless otherwise stated. Tests for mitochondrial activity (1-(4,5-dimethylthiazol-2-yl)-3,5-diphenylformazan, MTT) and production of an inflammatory mediator (interleukin-8, IL-8) were performed on both cell lines (HDF and A549) and done in triplicate. The pristine TiO_2 particles and the powders worn from the formulated TiO_2-enabled paint on drywall were exposed to cells at the concentration mentioned above.

3 RESULTS

Results show that the physical, chemical, and cytotoxicological characterization of the pristine TiO_2 particles was similar as previously published works [4, 5]. The physical data, such as size, was measured to be between 100 and 200 nm in diameter. The crystal structure of the materials were rutile, and the surface charge was slightly negative. Furthermore, the cytotoxicological evaluation after exposure to the pristine TiO_2 particles showed a dose-response in viability and IL-8 expression, where 100 ppb resulted in the LC_{50} values, on average.

However, powders of the formulated TiO_2 paint were significantly different from the pristine samples. Size ranged 1 to 5 μm and surface charge was neutral. The crystal structure of the TiO_2 particles in the composite was

rutile (i.e. same as pristine unformulated TiO_2; however, the latex surrounding the TiO_2 particles was not crystalline. Therefore, the surface reactivity was different as shown by Vitamin C degradation assay. Pristine TiO_2 degrades Vitamin C faster than the formulated TiO_2.

The cytotoxicological results of these tests showed that the formulated TiO_2 powders were less cytotoxic than the pristine TiO_2 particles. While identifying the exact hazards associated with exposure to formulated TiO_2-enabled paints and other composited materials cannot be determined using cell culture (i.e. HDF and A549) system, the *in vitro* model does serve the purpose to compare the potential toxicological responses of the material if exposures occurred via dermal or inhalation routes. More sophisticated tests are needed to accurately assess the risk, including exposure assessments of the aerosolized materials, dosimetry measurements within the cell cultures, and implementation of co-culture systems including macrophages and dendritic cells to assess immune and inflammatory biomarkers.

Data are presented as mean ± standard deviation. An ANOVA followed by a Dunnett's test was used to determine significance. The single factor ANOVA test was applied specifically to the samples used in a particular study as well as each dilution of the sample being tested. Statistical significance was established as $p<0.05$. All statistical tests were performed with excel software (Analysis Toolpak for Microsoft Excel).

4 CONCLUSIONS

This paper presents a methodology for performing a product life cycle analyses for engineered nanomaterials incorporated into specific construction coating materials, namely paint. The methodology, however, is applicable in a wide range of nano-enabled products including lacquers, structural composites, cements, and fabrics. Data shows that the physical, chemical, and toxicological properties of TiO_2 nanoparticle in their pristine, unformulated state is different than the properties after incorporation into the product. The implications of this research are: first, characterization of pristine materials may not be representative of materials when in a composited or other formulated form; therefore, information on the eventual fate of formulated materials must be obtained in parallel to information on the raw material. Second, the biological effects of formulated TiO_2 particles may be safer than the previously observed toxicological effects of TiO_2 nanoparticles.

5 TABLES AND FIGURES

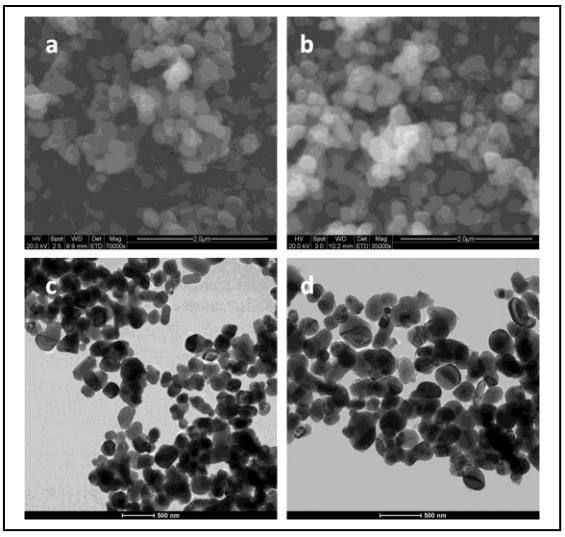

Figure 1: Representative electron micrographs of the pristine TiO_2 nanoparticles. A & B are scanning electron micrographs. C & D are transmission electron micrographs.

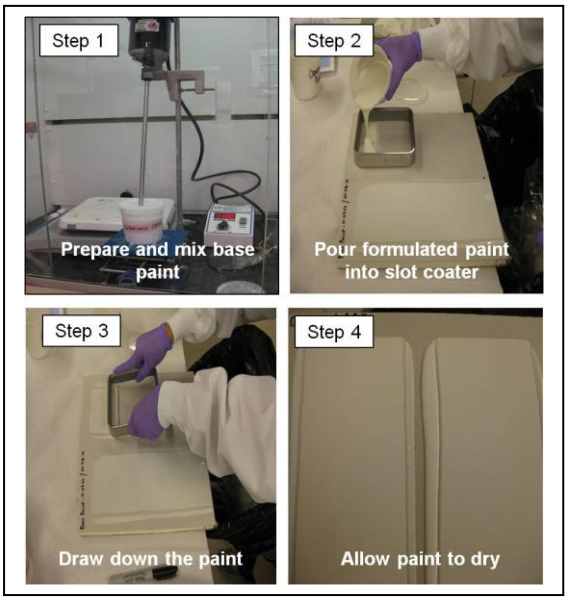

Figure 2: Pictures of the paint formulation process.

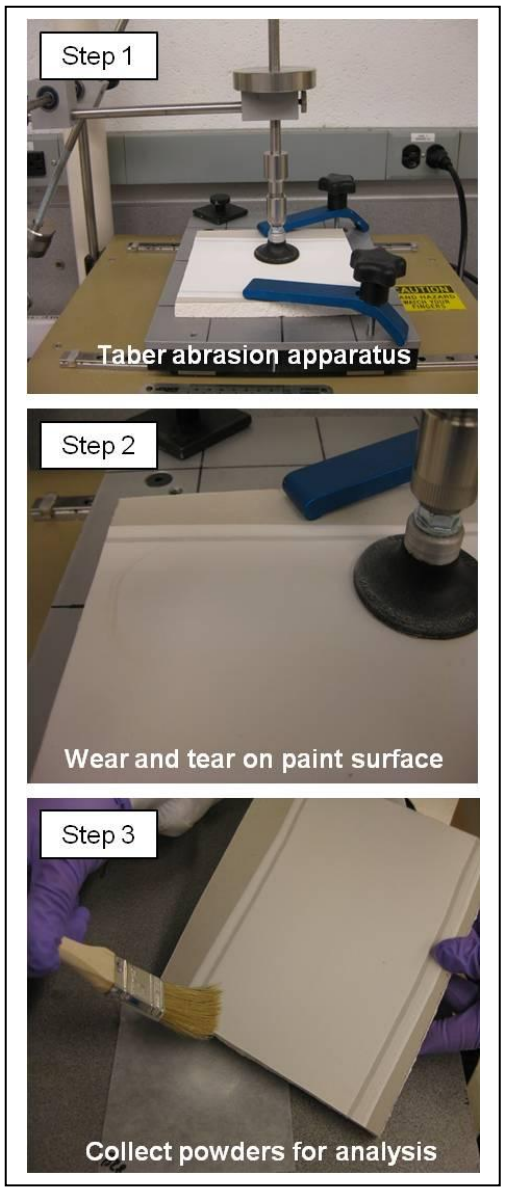

Figure 3: Pictures of the "wear-and-tear" process.

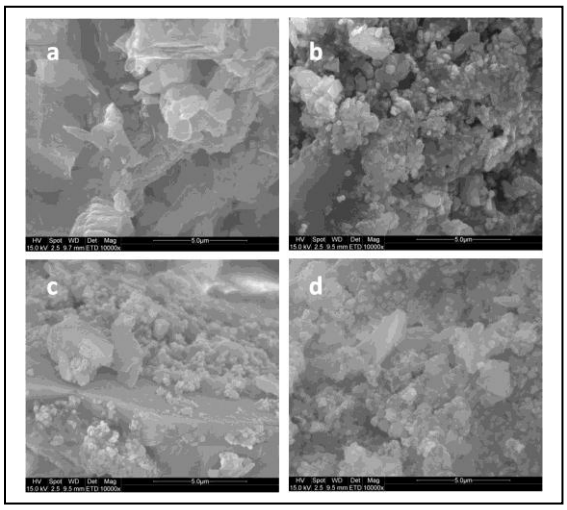

Figure 4: Representative scanning electron micrographs of powders worn from the formulated TiO_2-enabled paint on drywall.

6 ACKNOWLEDGEMENTS

The authors thank RTI International for funding this work through an internal research and development grant.

REFERENCES

[1] The World Market for Nanocoatings, *Future Markets, Inc.* November 2011.

[2] Taber abrasion standards DIN53754:1977,DIN68861-2:1981, ISO 5470-1:1999 and ASTMD4060-95:2007.

[3] M. Vorbau, L. Hillemann, M. Stintz, Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings, *Journal of Aerosol Science*, 40:3, 209-217.

[4] C.M. Sayes, R. Wahi, P.A. Kurian, Y. Liu, J.L. West, K.D. Ausman, D.B. Warheit, V.L. Colvin. (2006) Correlating Nanoscale Titania Structure with Toxicity: A Cytotoxicity and Inflammatory Response Study with Human Dermal Fibroblasts and Human Lung Epithelial Cells. *Toxicological Sciences* 92(1), 174–185.

[5] D.B. Warheit, R.A. Hoke, C. Finlay, E.M. Donner, K.L Reed, C.M. Sayes. (2007) Development of a base set of toxicity tests using ultrafine TiO_2 particles as a component of nanoparticle risk management *Toxicology Letters* 171, 99–110.