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Nanosilver conductive ink: A case study for evaluating the potential risk of nanotechnology under hypothetical use scenarios

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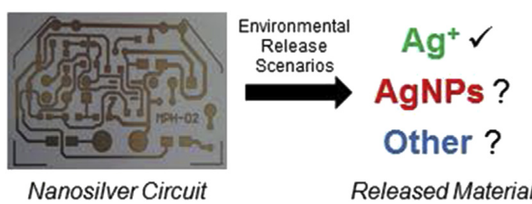
HIGHLIGHTS

- The release of silver and associated hazard from a nanosilver-containing electrical technology was assessed.
- A tier-based approach was used to guide EHS testing of the nanosilver ink and printed circuit.
- Aqueous exposure following disposal was identified as a likely release scenario.
- Silver released from printed circuits was primarily ionic.

GRAPHICAL ABSTRACT



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ABSTRACT

Engineered nanomaterials (ENMs) are being incorporated into a variety of consumer products due to unique properties that offer a variety of advantages over bulk materials. Understanding of the nano-specific risk associated with nano-enabled technologies, however, continues to lag behind research and development, registration with regulators, and commercialization. One example of a nano-enabled technology is nanosilver ink, which can be used in commercial ink-jet printers for the development of low-cost printable electronics. This investigation utilizes a tiered EHS framework to evaluate the potential nano-specific release, exposure and hazard associated with typical use of both nanosilver ink and printed circuits. The framework guides determination of the potential for ENM release from both forms of the technology in simulated use scenarios, including spilling of the ink, aqueous release (washing) from the circuits and UV light exposure. The as-supplied ink merits nano-specific consideration based on the presence of nanoparticles and their persistence in environmentally-relevant media. The material released from the printed circuits upon aqueous exposure was characterized by a number of analysis techniques, including ultracentrifugation and single particle ICP-MS, and the results suggest that a vast majority of the material was ionic in nature and nano-specific regulatory scrutiny may be less relevant.

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1. Introduction

Engineered nanomaterials (ENMs defined as materials with at least one dimension between 1 and 100 nm (National Nanotechnology Initiative, 2013) can provide a variety of advantages over bulk materials with regard to physical, chemical, and

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biological properties and as a result are being incorporated into a rapidly growing number of consumer products (Kessler, 2011; Project on Emerging Nanotechnologies). The understanding of the potential health and environmental risks of ENMs, however, has generally not kept pace with their increased utilization (Maynard, 2006; Klaine et al., 2012; Sharifi et al., 2012). A dearth of broadly accepted test methods and challenges associated with the unique properties of ENMs can make data collection and risk assessment difficult (Linkov et al., 2009; Klaine et al., 2008; Collier et al., 2015; Wardak et al., 2008; Petersen et al., 2015). For these and other reasons, regulatory guidance for the use of ENMs is lacking (Davies, 2009; Breggin, 2005; Pettitt and Lead, 2013; National Research Council, 2013).

Silver nanoparticles (AgNPs) are currently one of the most commonly used ENMs in nano-enabled technologies. The antimicrobial properties of AgNPs have been known for over a century (Nowack et al., 2011), and AgNPs have been incorporated into a wide variety of consumer products including clothing, food containers, and air purifiers (Project on Emerging Nanotechnologies). AgNPs have also been utilized for several electronics applications including optics (Lal et al., 2007) and printable circuits (Lee et al., 2006); ink-jet printing of conductive nano-inks has enabled the development of low-cost circuits using commercially-available printer technology (Finn et al., 2015). Due to its widespread usage and known toxicity characteristics, much concern has been raised over the health and environmental impact of technologies containing nanosilver and the need for their regulation (Hansen and Baun, 2012; Massarsky et al., 2014; Seltenrich, 2013). These concerns have led to a number of lawsuits being filed against the US EPA for approving the use of these nano-enabled technologies in consumer products with insufficient data (National Resources Defence Council, 2012; Center for Food Safety, 2015).

Recently, we proposed a tier-based approach to the evaluation of exposure and hazard potentials of nano-enabled technologies to support risk assessment and regulatory guidance regarding these technologies (Fig. 1) (Collier et al., 2015). This framework seeks to help determine when nano-specific scrutiny of a technology is or is not warranted, with a focus on relevant and useful testing for enabling risk decisions while deprioritizing testing that has lower relevance or impact on making a risk-informed decision. In Tier I, a technology is characterized and categorized using a system that considers not only the size of the ENM but how it is incorporated in the technology (i.e. surface-bound or embedded in a matrix) (Hansen et al., 2007). Both the size of the ENM and its properties that are unique from the bulk material are considered in determining whether a technology should be considered 'nano' and thus subjected to further nano-specific scrutiny. Once a technology is deemed to merit nano-specific testing, Tier II of the framework seeks to determine the potential for nanomaterial release during normal use (the relevance of other stages of the technology life cycle should also be considered). This is a critical, although often overlooked, step in the risk assessment of nanotechnologies (Brame et al., 2015); the hazard of the ENM alone may have little relevance if it is never released from the technology (Froggett et al., 2014). Furthermore, the released material must be thoroughly characterized, as the same forces responsible for its release may physically or chemically transform the ENM and change its potential hazard (Nowack et al., 2012). Tiers III and IV then serve to further inform the risk assessment of the nano-enabled technology by determining the environmental persistence (i.e. exposure potential) and toxicity (i.e. hazard potential), respectively, of the released nanomaterial.

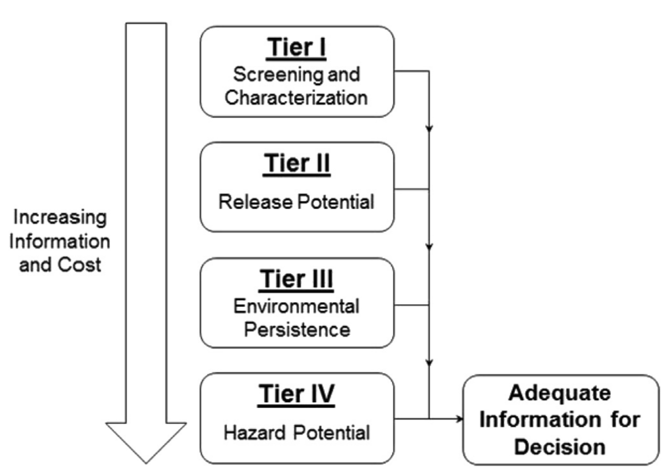

Fig. 1. Flow chart of our tier-based approach to the evaluation of exposure and hazard potentials of nano-enabled technologies.

In this work, conductive nanosilver ink was used as a case study to evaluate the efficacy of the framework discussed above. Both the as-supplied ink and printed material were fully characterized and, after being determined to merit nano-specific scrutiny, the printed material was subjected to submersion tests with and without UV light exposure to evaluate the potential for AgNP release. Since the release potential of a printed circuit during actual use is low, these tests were designed to roughly approximate the environmental exposure from a scenario in which an end-user disposes of a printed circuit. Since this case study is intended to evaluate and demonstrate the decision framework presented in Collier et al. rather than perform a thorough risk assessment, simulated circuits were simply submerged and shaken in water as opposed to more complicated testing that would more closely simulate rainfall or exposure to other natural waters. The potential for environmental persistence and toxicity (using the standard freshwater model *Ceriodaphnia dubia*) were then determined for both the as-supplied ink and the released material. Although more testing would be necessary to perform a true risk assessment of the entire life cycle of the technology, the results presented here demonstrate the applicability and utility of our tier-based approach toward normal use scenarios.

2. Materials and methods

2.1. Nanosilver ink

A conductive ink development kit (9102 Conductive Ink) was obtained from Methode Development Company (Harwood Heights, IL). Simulated circuits were generated by printing 4 cm × 4 cm grids (see Figure S1) onto 3G PET paper ('enhanced adhesion', obtained from the supplier) as directed in the user manual. Methods for microscopy and dispersion stability studies can be found in the Supporting Information.

2.2. Scanning electron microscopy (SEM)

High-resolution SEM images were obtained using an FEI Nova NanoSEM 630 Environmental Field Emission scanning electron microscope. Silver films were printed as described above and allowed to air dry overnight prior to imaging. The as-printed films were conductive and were thus imaged directly under high vacuum with no sputter coating. Accelerating voltages of 5–15 kV and spot sizes of 3.0–5.0 were used. Images were collected at 40, 100, 250 and 1000 k× magnification.