Nanosilver – Why It is Still So Hot?

K. W. Lem^(1a), J.R. Haw⁽¹⁾, D.S. Lee⁽²⁾, Z. Iqbal⁽³⁾, A. Salama⁽⁴⁾, R. Senthil Kumaran⁽⁵⁾, S. Sund⁽⁶⁾, S. Curran⁽⁷⁾, C. Brumlik⁽⁸⁾, and A. Choudhury⁽⁸⁾

(1) Department of Materials Chemistry and Engineering, Konkuk University, Seoul, Korea

(a) (O) 02-450-3497; (FAX) 02-444-3490; (email) kwlem@konkuk.ac.kr

(2) Department of Chemical Engineering, Chonbuk National University, Chonju 561-756, Korea suitable biocides

(3) Department of Chemistry and Environ Science, New Jersey Institute of Technology, NJ, USA.

(4) Department of Environmental Engineering, Konkuk University, Seoul, Korea

(5) Department of Microbial Engineering, Konkuk University, Seoul, Korea

(6) Nygard Consulting, LLC, NJ, USA

(7) Boston Scientific, MA, USA

(8) Nanobiz, LLC, NJ, USA

ABSTRACT

The safety of nanosilver (AgNP) is a potential "Nano-Titanic" preventing a sustainable nanosilver industry. Nanosilver effectively kills bacteria and is therefore biocidal, but many scientists are still uncertain of its safety to humans. Thus, safety has become a very sensitive and potentially critical issue for companies that make products containing nanosilver. On one hand, Senjen et al. [1] of Friends of the Earth claim that nanosilver is an extreme germ killer which presents a growing threat to public health. On the other hand, Volpe [2] and Height [3] of Silver Nanotechnology Working Group (SNWG) argued that AgNP used in antimicrobial applications is identical to all EPA-registered silver products for decades. Verv recently. Nowack et al [4] urged the policy regulators not to hastingly to declare nanosilver materials as new chemicals in their study on 120 years of nanosilver history.

Nevertheless, the German Federal Institute for Risk Assessment (BfR) recently conducted the Delphi study regarding nanoscale silver compounds in food products, cosmetics and every day products. To ensure that products are safe for consumer health, BfR recently recommended that German manufacturers not use nanoscale silver or nanoscale silver compounds in foods and everyday products until the data are available and comprehensive enough to allow a conclusive risk assessment [5]. Today, about 320 tons/year of AgNP have been produced and used worldwide [4]. Therefore, whether it is an old or new problem, we must deal with it seriously.

Keywords: nanosilver (AgNP), life cycle, exergy, triz in dfss (dflss-g), waste minimization, IP, Landscape.

1. PREVIOUS STUDY

To assess the safety of nanosilver at Konkuk University, we have begun our journey to study the life cycle

assessment of nanosilver starting with the use of product life cycle process mapping and Design for Lean Six Sigma with TRIZ. In our early work [6,7], we highlighted our literature research findings in the life cycle assessment of AgNP. We have applied exergy analysis, concepts of using TRIZ in Design for Lean Six Sigma - "Green" (DFLSS-G) to suggest the needs to have more multidisciplinary and international interactions to the characterization of AgNP products, their transformations in relevant biological and environmental media, in addition to systems and life-cycle approaches to nano-safety with a close collaboration between toxicologists and engineers.

2. GENERAL APPROACH

A significant potential issue is the impact of nanosilver on the environment. A rigorous material flow analysis is needed to quantitatively assess the environmental impact of AgNP emission. We have continued to use TRIZ to develop innovative concepts for eco-products research and development to minimize the use of nanosilver with maximum biocidal effect. Currently, we are focusing on Korean consumer products that contain AgNP because we found in our IP study, Korea leads in nanosilver applications among all major patenting countries. Major patent activity has been seen in the area of pharmaceuticals, consumer goods, semiconductor devices, preservatives, sterilization and water treatment. In this paper, we also discuss the highlight of a novel material design concept in eco-products development. Input to optimize at the control of release, the size, locality vs. totality, smart design of functionality during the release, came from a team consisting of chemists, toxicologists, microbial. environmental, biomedical, chemical engineers.

3. INTELLECTUAL PROPERTY

Intellectual property (IP) analysis of AgNP provides information regarding the direction of investment, technology development, competitive position, and possible future opportunities. Conducting an IP landscaping will provide an understanding for the patent opportunities, helped to assess new commercialization opportunities, and to design better eco-products containing AgNP. We have used Thomson Innovation database for the IP search. Several observations were found in a total of 5068 patent families from January 1, 1980 to April 5, 2011:

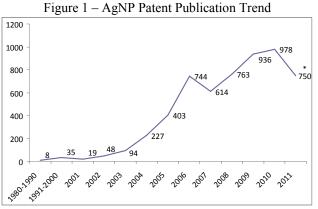
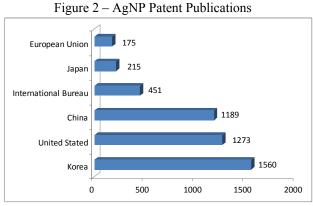


Fig.1 shows that patent publications in this decade with a growing trend has reach 978 publications in FY2010 and estimated at 750 in 2011. Amazingly in Fig. 2, out of all major patenting authorities Korea is leading with 1560 publications.US is on the 2^{nd} position and China is the third.



Due to its antiseptic nature of Ag, major patent activity in AgNP in Fig.3 is seen in the area of pharma and consumer goods, semiconductor devices, preservatives, sterilization and water treatment.

No surprise in Fig. 4, the main applicants across the world such as Samsung, LG, Xerox, Daewood, and Eastman Kodak have been investing heavily in AgNP.

4. RELEVANT AgNP IP SPACE

Using the IP Landscape analysis, we have identified relevant IP in the space of pharma and consumer goods patents. Intensive IP analysis, such as broadness of claims, details of office actions can help in identifying the share of the market that can be attributed to current and future technology. Active companies in the technology space were identified as they can influence the market captured by the current "eco-product" similar. For example, LG Household and Health Care Ltd (health cares) and L'oreal (cosmetic) are amongst the major assignees for in the space of pharma and consumer goods patents.



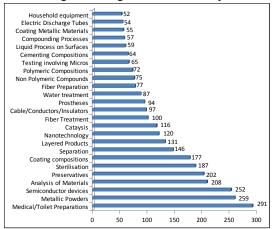
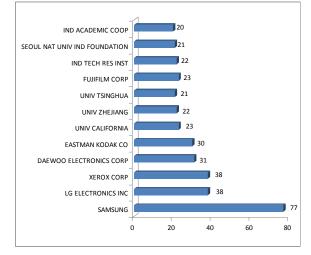


Figure 4 – AgNP IP Key Global Players



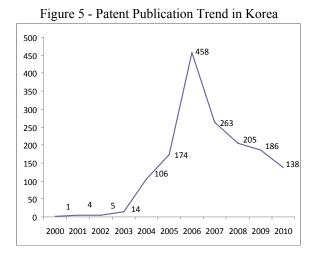
5. HOW HOT AgNP IP IN KOREA

A good measure of how hot the technology is the investment in its IP protection. Korea that has invested enomously is leading with 1560 publications among major patenting countries. As seen in Fig. 5, Her AgNP IP activities began at 2000 with 1, peaked at 2006 with 458, then dropped to 138 in 2010. The major reason for the drop is probably due to the unkown toxicity. Thus, safety has become a very sensitive and potentially critical issue for companies that make products containing nanosilver.

6. PRODUCTS CONTAINING AgNP

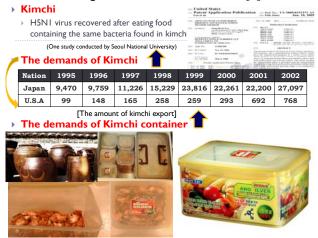
Nanoproducts can be made in two ways: top-down and bottom-up. A top-down approach is essentially tearing

down of a device to gain insight into its components, materials and compositions. A bottom-up approach is the piecing together of materials to give rise to components and finally to build a device. Commercial AgNP products are very likely produced by a bottom-up process, whereas analysis of environmental impact by AgNP products is a top-down process [6,7]. Unlike



most inert materials, it has been known for centuries that silver has an antiseptic effect.

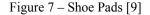
Figure 6 - Kim Chi Containers [8]



Koreans have also chosen silver to make their metal chopsticks. Recently, silver has found use in everyday products such as antimicrobial products, consumer products, and electronic products. The antiseptic effect gives an extra dimension in dealing with the life cycle assessment of silver. Nanosilver can be made with different shapes such as particles, wires, and rods. Due to its enormous surface reactivity, AgNP found use in Korean everyday products as in Figs. 6-7 that require antibiotic performance, such as food contact materials, textiles and fabrics, appliances, consumer products, children's toys, infant products, 'health' supplements, cosmetics and pharmaceuticals [5-8]. Using energy dispersive X-ray spectroscopy (EDX) analysis [4], we have found that not all the commercial products claimed to have AgNP indeed contain AgNP [8, 9].

7. DFLSS-G AND TRIZ

We have recommended earlier [5] to use use design for LEAN SIX SIGMA- GREEN (DFSS-G) and TRIZ to design eco-products. Kobayashi [10] has used a product life planning methodology based on a quality function deployment (QFD) and a software tool to establish an *eco*-design concept of a product and its life cycle in multigenerational eco-products development. Serban et al.[11] have used a triz approach to design for environment for over a product life cycle. We need to answer the following three hard questions in this design:





- 1. Do we have a complete understanding of AgNP product life cycle?
- 2. Do we have a clear understanding on the unmet needs?
- 3. What can we do to minimize use of AgNP with optimal effects?

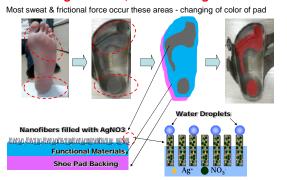
We have started to answer the first question by examining each step of the material flow in a metabolism during the life cycle. The value generated is equal to the food resource available in each step minus the wastes at each step[5]. In the material flow model, we will include probabilistic method as suggested by Gottschalk et al [12] that is commonly being used in DFSS. To answer the second and third question, we need to understand how the use of nanosilver can be minimized based on specific needs in locality, time/control of AgNP release mechanisim.

8. SHOEPADS-CONTROL OF RELEASE

It is well established that the size of nanomaterials affects its properties[13], and there is no exception in

AgNP, particularily as an antibacterial and antibiofowling agent [14-18]. Bacterial fowling on human has become a serious environmental and health implication. The existence of bacteria and its fowling in shoes and socks used/worn by

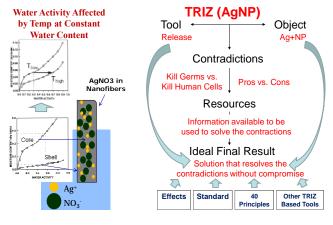
Figure 8 – Control/Time of Release in Shoe Pads Controlled Release of AgNP and Ag+NP by Controlling Location, and Water/AgNO3 Release



human can lead to problems such as biofouling accumulation which lead to health problems. However, as seen in Fig. 8, only certain areas in shoe pad may require suitable biocides such as AgNP for antifouling. The amount of AgNP release depends on the mechanics of the release. To prevent and control these occurrences, it is necessary to use "right amount" of suitable biocides to control fowl and kill microbes. Using a TRIZ approach [19] in Fig.9, such a concept is proposed to use water activity as a means to control the water content of AgNO₃ in the nanofibers where these nanofibers have a shell and core structure. In addition to the controlled release of AgNP, the use of the nanofibers is to produce a very high contact angle surface to prevent water absorption on the surface (i.e., the Lotus Leaf Effect). In the future, we will conduct a DOE for an in-vitro study to evaluate the microbial (population/) growth (bacteria) in the used shoe-pads with the controlled release of AgNP. We will continue to report highlight from our future study.

Figure 9 – The Proposed TRIZ Concept

Using Water Activity to Control the Water Content of $AgNO_3$ in Nanofibers with a Core and Shell Structure



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