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Nanotechnology: Implications for the Wood Preservation Industry

Carol A. Clausen

USDA Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison, Wisconsin 53726 USA

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IRG Secretariat
Box 5609
SE-114 86 Stockholm
Sweden
www.irg-wp.com

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Carol A. Clausen

Supervisory Microbiologist, USDA Forest Service, Forest Products Laboratory[1], Madison, Wisconsin, USA 53726. E-mail: cclausen@fs.fed.us

ABSTRACT

Nanotechnology has the potential to greatly impact the wood protection industry through the creation of nanomaterials with unique properties. Nanobiocides may find applications as co-biocides, or may alter treatability properties such as penetration and biocide distribution. Nanocarrier delivery systems may increase the applications for organic biocides through controlled release of biocide, treatment of engineered composites with heat-labile biocides, or prevention of leaching in otherwise soluble biocides. The unique properties of nanomaterials that make them attractive as preservatives may also present unknown and unpredictable risks. Investments by the National Nanotechnology Initiative are directed at research on environmental and health risks. Development of an International Risk Governance Council aims to provide recommendations for assessing the risks associated with nanoproducts before they enter the marketplace.

Key words: nanotechnology, nanoparticle, nanotubule, nanobiocide

[1]The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

1. INTRODUCTION

The U.S. National Nanotechnology Inititative (NNI) is a long-term national research and development effort to explore the fundamental knowledge of matter at the nanoscale, to develop fundamentally new applications for nanoscale phenomena, and to begin industrial prototyping and commercialization of nanotechnologies. The United States NNI program began in 2000 and was the first and largest program in this new discipline. Since NNI's inception similar national nanotechnology R&D programs have been announced by Japan (April 2001), Korea (July 2001), EC (March 2002), Germany (May 2002), China (2002) and Taiwan (September 2002) (Roco 2006). The initial role of government R&D, which is that of basic research, continues while industrial R&D moves towards development of new applications.

In 2004, a workshop on Nanotechnology for the Forest Products Industry was held with the purpose of identifying key issues that nanotechnology can address for the Forest Products Industry. Among the sponsors of the workshop were the American Forestry & Paper Association (AF&PA) and USDA Forest Products Laboratory. The result of the workshop was a published Vision and Technology Roadmap (2005) developed by sponsors and participants, which is available on the Forest Products Laboratory website (www.fpl.fs.fed.us). What's in the roadmap for the wood protection industry? Their vision includes utilizing nanotechnology to revolutionize product offerings. Key strategies include adapting and deploying added value and functionality to existing products as well as creating and deploying novel new nanotechnologies that enable new generations of cost effective products. One priority of the roadmap is to use nanomaterials to improve the raw material. Utilizing nanotechnology to enhance durability and resistance to moisture and decay addresses this vision. Their key strategies have always reflected our key strategies. Our charge is to develop and evaluate applications for nanomaterials in the context of wood protection.

There is no universally accepted definition of nanotechnology and researchers often use the term to cover any research, process or production at the nanoscale (Bottiglieri 2006a) Nanotechnology is more specifically the development and application of materials, devices and systems with fundamentally new properties and functions because of their structure in the range of 1 to 100 nanometers (Siegel et al. 1999). Size, properties, and function dictate whether a research outcome is truly nanophenomenon.

The NNI predicts four stages of nanodevelopment will take place during the nanotechnology revolution:
Stage 1 or the first generation of nanotechnology includes development of passive nanostructures involving the development of new materials with unique properties and functions that would be used as part of a product (Roco 2006). This stage might involve the development of coatings, films, nanobiocides or reinforcing nanofibers in new composite products. The first stage began in 2000 and will continue indefinitely as the field of nanotechnology evolves.

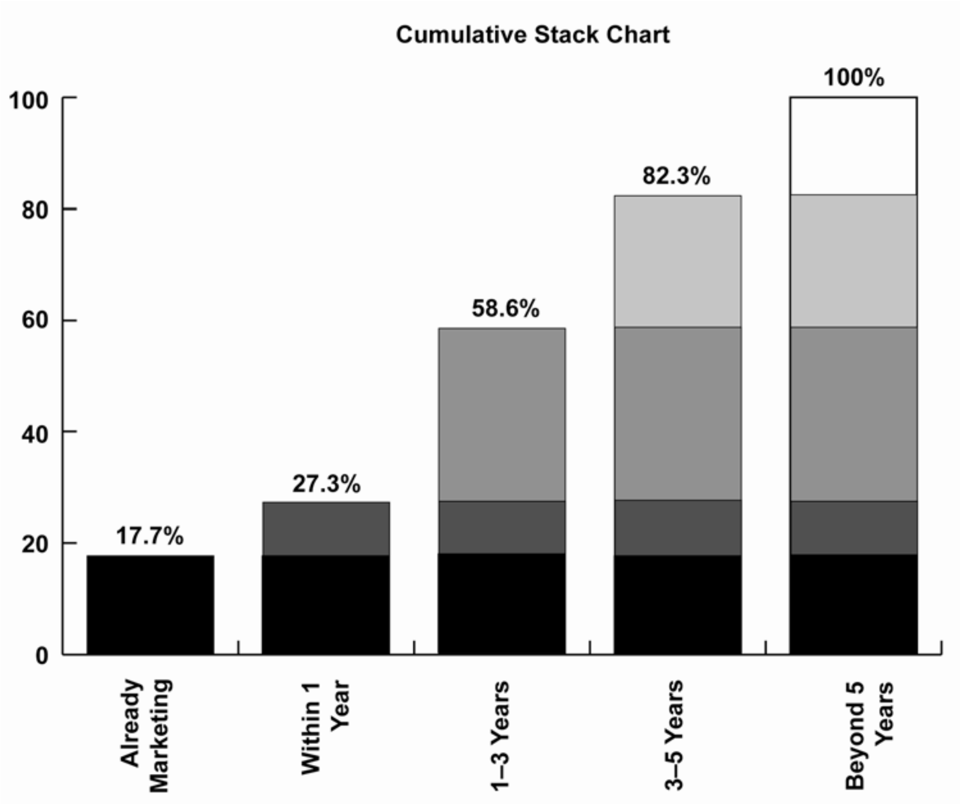

Figure 1. Year 2000 estimation of worldwide markets incorporating nanotechnology. Adapted from Roco and Bainbridge (2001).

The second stage or second generation began in 2005 and involves the development of nanostructures that can change shape, size, conductivity or other properties during their use (Roco 2006). Applications involve targeted delivery systems for drugs or nanodelivery systems for preservatives.

Stage three (i.e. third generation nanotechnology) is expected to begin around 2010, when nanocomponents will form specified end products. Examples of nanotechnology at this stage of development include self-assembly of three-dimensional devices such as networks and guided assemblies or novel robotic devices**.**

From the year 2010 to 2015 and beyond, (Stage 4) nanotechnology will expand to include molecular nanosystems, heterogeneous networks in which molecules and supramolecular structures become distinct devices with self-assembly capabilities (Mehta 2005; Roco 2006). An example of this stage might be extraordinarily small robotic devices or molecular nanosystems that could operate at a high rate of speed over a wide range of environmental conditions.

R&D Investments

Government investments worldwide for nanotechnology R&D have increased from $825 million in 2000 to $4.1 billion in 2005. With an increased recognition of nanotechnology by CEOs, all Fortune 500 companies made investments in nanotechnology after 2002. Of the 1,455 US nanotech companies in business in March 2005, roughly half were small businesses; new nanomaterials and products are in the development stage at both small and large companies. Twenty-three thousand new jobs were created in start-up nano companies, and the NNI Small Business

Innovation Research (SBIR) program invested $80 million in small businesses in 2005.

In 2000, only 1% of companies reportedly had a corporate interest in nanotechnology. According to a 2005 survey by the National Center for Manufacturing Sciences, 18% of companies surveyed are marketing a nanoproduct (Figure 2). Eighty percent of all companies are expected to have nanoproducts by 2010 (Roco 2006). Currently, major application markets include coatings, paints, thin-films, particulates, nano-structured particles and nanotubules followed closely by drug delivery and diagnostic systems, and medical implants. The trend is in "designer" (i.e. application-specific) passive nanomaterials. In the near future, we can expect to see improved reliability, efficacy, safety, performance and economic feasibility in such products.

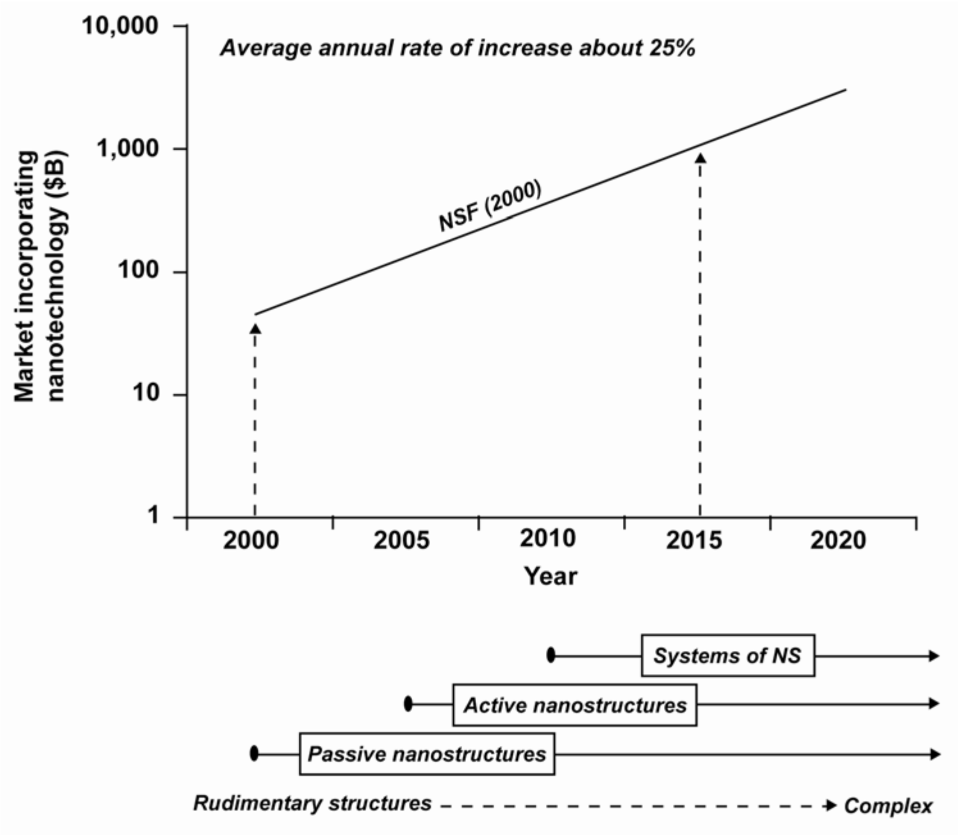

Figure 2. Timeline for growth in commercialization of nanoproducts (Mehta 2006).

NNI's vision of a grand coalition is taking shape. In the United States, seventy universities and 12 government laboratories have created significant nanotechnology user capabilities (Roco 2006) linking users with facilities through user networks created by federal entities such as National Science Foundation (NSF), National Institutes of Health (NIH), Department of Energy (DOE), National Aeronautic and Space Administration (NASA), Department of Defense (DOD), National Institute of Standards and Testing (NIST), and Center for Disease Control (CDC).

Public Perception

Great waves of skepticism have haunted nanotechnology from its inception. Between 1990 and 2000, nanotechnology suffered from a concern about its true relevance as a field of scientific study and from pseudoscientific claims (Roco 2006). Despite development of nanomaterials and commercialization of nanoproducts, there remains a level of scientific skepticism for future products we can only vaguely imagine. Next came fear of the unknown and concern of unexpected consequences, dubbed the "grey goo" scenario (Bottiglieri 2006). A National poll conducted in September 2006 by the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars in Washington D.C. reported that only 30% of Americans have heard something about nanotechnology, which was a considerable increase from 16% in 2004. Respondents had heard of nanotech in terms of products used in sunscreen, golf clubs or stain resistant pants. Of those respondents that claim to have heard little about nanotechnology, 35% saw more risks inherent in nanotechnology and 15% saw more benefits. Almost half of those that claimed to have heard a great deal about nanotech saw more benefits. But of those respondents that had never heard of nanotechnology, only 2 % favored benefits of nanotech over risk.

Familiarity with nanotechnology terminology, product recognition and acceptance are the first steps in consumer education, but fears regarding safety of nanoproducts need to be scientifically alleviated. The next wave of concern over environmental health and safety implications began in 2002 as industrial development increased. Government-funded R&D initially involved high-risk basic research that could be transferred to industry for product development.

Environmental Concerns

The risks inherent in nanotechnology may exceed the normal risks encountered with a new field of science. Nanotechnology innovation is proceeding ahead of the policy and regulatory environment (Renn and Roco 2006). The NNI invested about 4% of its 2006 budget for research exploring the potential environmental and health risks associated with nanotechnology (Bottiglieri 2006b).

The International Risk Governance Council (IRGC) established in 2005, provides the following recommendations for the risk governance of the first generation of nanoproducts:

1. testing strategies for assessing toxicity and eco-toxicity
2. best metrics for assessing particle toxicity and eco-toxicity
3. research on disposal, dispersion, and water treatment of nano-engineered materials
4. exposure monitoring methods (i.e effectiveness of glove boxes, hoods, air filters)
5. evaluate the probability and severity of risk for nanotech applications
6. risk assessment methodologies
7. communication and education concerning ethical, legal and social issues

Pharmaceutical and biotechnology companies that are taking a wait-and-see attitude on nanotechnology, may reflect the general attitude of industry (Morrow 2006). Little data exists on the human health impact of nanomaterials, although they have been used commercially in applications such as stain-free clothing and sunscreen. Research efforts include those involving the impact of airborne nanoparticles on occupational health and their possible impact on human exposure, including toxicity, inflammation, cancer and respiratory illness. Will nanoparticle-based preservatives or coatings cause an increased risk to human health if treated products are fabricated on a construction site or sanded by a home-owner? It was recently reported that carbon nanotubes, which are normally hydrophobic and clump together in water, interact with decomposed plant and animal matter in unfiltered water and disperse through the solution (look up reference 2006). This may raise concerns about carbon nanotube release by factories into rivers and lakes. In other applications, the same dispersion properties may be highly desirable. Therefore, concerns about environmental risks need to be properly evaluated during this exploratory phase of nanobiocide product development. Because nanomaterials, by definition, have unique properties that can be manipulated, risks associated with such new properties may be totally unrelated to the properties of the material from which the particles are derived. Toxicity risks and regulatory oversight will need to be developed to address this new set of properties, most of which are poorly understood at this point in time. To that end, the Environmental Protection Agency (EPA) recently decided to regulate all consumer items made from nanoparticles of silver. Previously, products containing nanoparticles of silver such as air-fresheners, food storage containers, odor controlling shoe liners, and washing machines have been considered “devices” and did not need regulatory approval. However, at least one trademark microfibre fabric used in athletic wear claims that silver particles inhibit bacterial growth to reduce unpleasant odours. Environmentalists argued that because nanosilver kills bacteria and aquatic organisms, it poses a risk to human health and should be considered a “pesticide”. The EPA maintains that it only intends to regulate products that make a claim to kill a pest as “pesticides”. Final ruling on regulation of products containing nanoparticles is pending.

Wood Protection Applications

Nanobiocides

Either used alone or in combination with existing biocides, nanometals may provide the basis for the next generation of wood protection products. To date, few reports exist on the efficacy of nanometal preparations as biocides. Silver exhibits a broad range of antimicrobial activity against gram-positive and negative bacteria, yeast and molds (Kourai H. 1996). However, a report on ionic silver showed little effect on inhibition of decay and mold fungi in laboratory tests (Dorau et al. 2004). A study by Green and Arango, that evaluated silver formulations in combination with copper or zinc nanometals against termites, showed inhibition of termite feeding by zinc nanoparticles with and without silver (Green and Arango 2007). Silver nanoparticles constitute a reservoir for the antimicrobial effect. In the presence of moisture, metallic silver oxidizes, which results in the release of the silver ions. Silver ions are the species that are responsible for microbial inhibition. Because silver oxidation is a slow reaction, the size of silver particles is critical to achieve microorganism growth inhibition. The smaller the particle size, the higher the surface area, and the greater the area available for oxidation. Particles with diameter less than 100 nm are required to have the surface area necessary to allow a continuous release of silver ions. The main advantages of silver nanoparticles over organic biocides are: 1) non-volatile and non-degradable over time, 2) odorless and 3) long term efficacy.

Nanometals are created by altering particulate size either in the liquid phase (e.g. metal oxide sols, colloidal metals), gas phase (e.g. flame synthesis, plasma-based vapor phase synthesis) or solid phase (e.g. high energy ball milling) via chemical reaction, heating, or refluxing. Nanometal preparations of silver, zinc, copper, etc. have high dispersion stability and low viscosity allowing for more uniform particulate distribution over a surface. Dispersion stability coupled with controlled particle size may greatly improve:

1. Preservative penetration in commercial lumber species
2. Treatability of refractory wood species that are of low commercial value
3. Durability of engineered composites
4. Stability of finishes and coatings for above ground applications
5. Non-leachable or hydrophobic treatments

Nanocarrier delivery systems

Another development that bridges the first and second stages of nanotechnology, depending on the application, is nanocarrier delivery systems. Several carriers are recognized that may find application in the field of wood protection, particularly for increased durability of engineered composites (i.e. oriented strandboard). Laks (2005) patented a nanocarrier system that utilizes 100 nanometer plastic beads embedded with biocide. Based on type of polymer comprising the bead, pore size in the bead, biocide viscosity and solubility, biocide-embedded nanoparticles can be designed for slow, controlled release of the biocide. Other cylindrical, tubule-shaped materials (i.e. nanotubules) made from ceramics, clay, metal or lipids have been used as carriers in various medical and industrial applications. Some properties of nanocarriers that would benefit the field of wood protection include

1. Delivery and placement of biocide
2. Slow release of a biocide
3. Release of the biocide upon exposure to certain environmental conditions, such as high humidity
4. Protection of heat labile organic biocides during treatment processes or panel fabrication

Modes of delivery

Nanotubules may be surface coated or capillary loaded. Surface coated tubules can be layered with the chemical to form a barrier or the chemical may be entrapped on the surface of the carrier. The coating can be biodegradable or serve as a carrier system for a chemical that is released upon biodegradation. Chemical properties of the surface coating are important considerations when designing a nanocarrier system. Do they need to be hydrophobic, soluble or adsorptive to meet the needs of the system?

Nanotubules can also be capillary-loaded and that process is highly dependent on the internal diameter of the nanotubule, chemical viscocity and solubility as well as chemical reactivity to the nanotubule material. Capillary loading may rely totally on adsorption of the chemical. Resistance of physical forces is not only important to capillary loading of nanotubules, but is also important in the release of the treatment chemical, both intentional slow-release and unintentional leaching.

Loaded nanotubules may be used for surface application, pressure impregnation, or as an additive to engineered products, films, coatings or sealants. Some considerations include how to precisely control release of a biocide, whether the nanotubules are compatible with resin if used to treat composites, whether the resin itself may be a barrier to release of the biocide, the risk of release during finishing, refinishing, or sanding, calculating and regulating actual release rate, and development of methodology for analyzing release rate. Proper design could lead to increased applications for biocides that are otherwise unsuitable for exterior or in ground applications, including but not limited to soluble biocides, heat labile biocides and delivery of targeted nanobiocides.

4. CONCLUSIONS

Nanotechnological applications for the wood protection industry have great potential for improved treatability of refractory wood species, developing slow-release biocides for engineered composites and delivery systems for targeted biocides. We must proceed scientifically with cautious optimism and be mindful of the risk governance recommendations.

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