



The magic of nano

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While the production and handling of some nanoparticles are problematic, by and large the industry is hedging its liability by taking some precautions. The industry's greatest fear is that some product will be marketed and a disaster will ensue with consumers deciding to transfer the negative valence from this one product to all or nearly all nano-related products. While I believe the case for contagion is overstated, my greatest fear is that nanoparticles may be proven hazardous and the industry moves from countries in North America, Europe and Asia with strong occupational regulations to countries with weaker or nonexistent one, leaving government with the onerous task of adding trade rules. Consequently, it behoves us to be especially vigilant as new products enter the market.

When nanoparticles are incorporated into finished products, there is less concern, although it would be prudent to complete life cycle analyses especially at the disposal or reclamation end. What seems to concern many of us much more are free nanoparticles and aerosol nanomaterials. These products could be a major problem, whether we are using the nanoparticles for remediation or suspending them in an aerosol. While the remediation issue needs to be addressed, this article examines the second phenomenon, and that brings us to the subject of Magic Nano and what we can learn from this event.

Sonnenbühl, Germany-based Kleinmann GmbH, a subsidiary of the Fortune 500 company Illinois Tool Works, marketed its Magic Nano Bad WC Versiegeler earlier this year. Barely 4000 cans of the product were sold in Penny Market discount stores on March 27th before being taken off the market or recalled on March 28th after 97 people reported breathing problems, heavy coughing, trouble sleeping and 6 were hospitalized. The complaints were tallied mostly from telephone calls to poison control centres in Germany. It was reported that calls were also received in Switzerland and Austria via the European rapid alert system for non-food products known as RAPEX. Kleinmann announced there was expected to be no long-term damage and 12–18 hours after the event and the recall the complaints subsided.

On March 31st, Germany's Federal Institute for Risk Analysis (BfR) released a statement warning consumers about using the product in an enclosed area. Of course, as a bathroom sealant (given that bathrooms are mostly enclosed spaces), ventilation would be problematic.

Anecdotally, Kleinmann's windscreen cleaner and the pump version of the bathroom and tile sealants, which have been on the market for four years containing similar materials, have

not generated alarm. Of course, the windscreen product is used in well-ventilated areas and the second is not in aerosol form. In addition, it soon became apparent that there were two Kleinmann products involved. Both were glass and ceramic protective sealants and both were sold under the brand Magic Nano. The association of which product with what percentage of the complaints is still unclear. It seems likely they were bundled together because they were both recently sold in aerosol form.

BfR began to uncover the cause of the distress and the pulmonary oedemas. As soon as the pre-release was delivered into my mailbox, I sent it to most of the members of the Steering Committee of the International Council on Nanotechnology (ICON), on which I serve as Communications Director. This led to a statement from ICON suggesting care and vigilance.

Magic Nano is a product line and this specific product is a sealant. Kleinmann reported that their initial investigations found that the nano-liquid component of the spray was not to blame. The assertion made by Kleinmann about a nano-liquid caused some misunderstanding. The term has no scientific meaning *per se*. It is the product name for a suspension sold by Audiyo, which seems to be unlike the NanoPool product (see below).¹ A scientist from the company producing the liquid went on record that the liquid in question did not contain nanoparticles and this was subsequently verified by testing.

BfR held a preliminary meeting on April 7th with company representatives, toxicologists, pulmonologists, and others to discuss the implications, and came to inconclusive findings. Furthermore, the sealing liquid from NanoPool was tested on April 7th at Saarland and preliminary reports suggested the cleaner was not responsible for health problems. The *Economist* reported on April 10th that the product inside the aerosol can came from Hago and was cleared by BfR. Kleinmann recounted that Hago had reported that testing was completed.

Two components in the Magic Nano sealant that were not actually produced at Kleinmann were the aerosol and the sealant product. The source of the aerosol was Hago Chemotechnik GmbH & Co, part of the FLM-Group. Hago produces liquids for aerosol cans. The second component was a glass and ceramic liquid protection product from NanoPool. NanoPool has two related products that produce protective films. NanoPool Glass&Ceramic Protect Anti-bak is an anti-bonding coating that prevents the growth of bacteria, and NanoPool's website includes sanitized areas, such as hospital theatres, patients' bathrooms, etc. as application sites. NanoPool Glass & Ceramic Protect is recommended for use on window panes, solar glass panels, shower partitions, wash basins, tiles etc. There are no care instructions on the NanoPool website for these products.

As such, the liquid comes from NanoPool who subcontracted its formula and its manufacture to Easyglas. NanoPool claims it does not contain nanoparticles, while the aerosol product itself comes from Hago and the constituent components of the aerosol are unknown. Kleinmann combined the products and packaged Magic Nano as a home disinfectant and water and oil repellant sealant. Kleinmann wanted to introduce one of the first end-user nano-

¹ What is (a) Nano Liquid? Obviously it is a trade name for a suspension. For example, a product called Nano Liquid (see audiyo.com) is made up of gold and silver with particles in the 8 nm range held in suspension by mixing them with a controlled amount of squalene oil. Squalene oil is found in nature and its sources include olives, palm oil, wheat germ oil and shark liver oil, and is used as a moisturizer. The producers claim some conductivity advantages associated with their product.

products, foreseeing huge possibilities and future market potential, and expected a substantial return from Magic Nano.

Another complication came on April 14th. The Federation of German Consumer Organizations (vzbv) is an NGO acting as an umbrella for 39 German consumer associations. Chairwoman Edda Müller complained that Kleinmann used the seal of approval of a major German testing organization (TUV Sued) without authorization. The TUV Sued stamp reads: “Production Inspected, Safety Approved.” vzbv has reported the case to the district attorney and called for a criminal investigation against the manufacturer for suspected violation of the German Food, Household, and Animal Feed Law.

The *Economist*, like one of my early blog entries,² identified silicate particles suspended in a fluid as an important component of Magic Nano, but it is unlikely they were nanoparticles. When applied as a thin film, these silicates block micro-crevices, in turn reducing the scope for attachment of dirt, moisture and bacteria, and this function does not require nanoparticles.

Actually, we learned Magic Nano was a solution of perfluorated siloxane oil in ethanol (siloxanes are a class of both organic and inorganic chemical compounds that consist entirely of silicon, oxygen, and an alkyl group). Whether silicon was the sealant is addressed below. In an earlier blog, I suggested the cause might be the propellant. We learned the propellant was dimethyl ether (also used in hair sprays).

A spokesman from Kleinmann added another possibility, which was that the anti-corrosive liquid inside the propellant might have been the causative agent. For a while, there was no mention about the anti-corrosive used in the aerosol. However, we learned on April 4th that it was a phosphoric acid ester, which could be implicated. Reported symptoms for Magic Nano are quite similar to inhalation warnings on similar products using phosphoric acid esters.³

The inhalation of impregnation sprays is common. There were reports a few years ago associated with water repellants and other sprays with no nanoparticles and this recent event reads like a conventional inhalation attack, much like using aerosol spray paint in an enclosed area without any protection such as a mask.

In addition, the aerosol nature of the spray might have led to the causative agent reaching deeper into the lungs than it might have done in the pump spray version. The pump version is unlikely to produce droplets under 100 micrometres. On the other hand, aerosol products can generate droplets in the 10 micrometre range and that would be sufficient to penetrate deep into the lungs.

According to a recent article in *Photonics*, while BfR did explain that the size of the droplets were very small in the aerosol version of the sealant, which probably allowed the irritant to reach deeper into the lungs, it did not rule out that the culprits were nanoparticles in the droplets, especially when there seems to be a consensus that classical toxicological assessment of the individual components may not be adequate when examining the toxicological interactions that may occur on the nanoscale.

In the April 12th press release BfR was very cautious in its preliminary findings. “The lack of data on both toxicological properties and the nanoscale of the particles make it impossible to

² www.nanohype.blogspot.com.

³ MSDA Sheet for Starbrite Teak Cleaner, <http://www.starbrite.com/msdssheets/81416-msds-11-11-05.pdf>.

determine in a definitive manner whether the nanoparticles, a component of the aerosol, contributed to the health problems”.⁴ BfR was unwilling to confirm the presence of nanoparticles, as a component of the aerosol, due to the lack of data. BfR did add that the distributors of the spray were “unable to supply the full formulations because information was missing from upstream suppliers”, which is worrisome and independently may constitute a failure to comply with the Equipment and Product Safety Act. It is unclear whether the testing was completed on the Hago product independently or in combination with the NanoPool product, both of which came together in Magic Nano.

These concerns were laid to rest at a BfR meeting on May 23rd. Three days later, BfR reported that the Magic Nano products “do not, in fact, contain any nanoparticles.” This conclusion was drawn after a meeting of experts three days earlier and “was also confirmed by chemical analyses commissioned by BfR from two specialist laboratories”.⁵ The Verband der Chemischen Industrie (VCI), an industry trade association, ordered the analyses and BfR accepted their findings despite reservations over their independence.

In addition, René Zimmer from BfR added that “the stuff didn’t do what it was supposed to do.” In use, there is a rise in acidity, which may have prevented the anticipated sealant effect by a sol-gel process and may have produced silicic acid as a by-product. Presumably, the analysis did not find much silicon in the product, hence the sealant did not seal as advertised. Its oil and water repellant qualities seemed to have been exaggerated.

What have we learned

The first lesson has to do with causality. Without an established cause and effect, it is possible to inappropriately assign a hazard classification to a product of nanotechnology and by association an entire class of materials (more on this effect below). The case of Magic Nano is a classic example of this error, with the ETC Group and Anthony Seaton⁶ jumping the gun.

My apprehension rests on two observations from my review of the literature. First, there is excellent experimental data suggesting that remediation of some of our worst toxic waste sites might be possible with passive and functionalized nanoparticles. Second, there is some highly encouraging data suggesting that functionalized nanoparticles might be very effective in treating a set of cancers that are devastating the lives of millions of people.

False transference of effects across a spectrum of nanoproducts simply makes me cringe, especially when risk assessment of a nanoproduct is never done comparatively. While a nanoproduct might have some serious drawbacks, it might be much more desirable than the alternative. If the choice is between zero valent iron in nanoparticulate form and chlorinated solvents and methanogens, I would probably choose the former.

The next lesson has to do with naming of products and product lines. Why Magic Nano? One source argued that the film, meaning the surface layer, laid down when the product was used properly had a nano-sized thickness. BfR claimed on May 26th “the term “nano” in the

⁴ Federal Institute for Risk Assessment (BfR), “Cause of intoxications with nano spray not fully elucidated,” April 12, 2006, <http://www.bfr.bund.de/cms5w/sixcms/detail.php/7699>.

⁵ BfR, “Nano particles were not the cause of health problems triggered by sealing sprays?” May 26, 2005, <http://www.bfr.bund.de/cms5w/sixcms/detail.php/7842> (accessed May 26, 2006).

⁶ See <http://www.rsc.org/chemistryworld/News/2006/May/03050602.asp> (accessed May 26, 2006).

product names is intended far more to draw attention to the wafer-thin film that forms on the surface of glass or ceramic after the spray application of the products.”

The uncertainties associated with this recall underscore the need for clarity with respect to terminology, hazard identification, and risk communication. The nano prefix is being abused by advertising and marketing people and needs to be reined in. While there seems to be only one reported instance, involving NanoTex, where a decision was made to rescind the nano moniker from a product line, there are many more cases of the reverse. “Nano” remains a marketing term that adds value to a brand name. By reducing the size of particles, a product can be remarketed as enhanced and improved and the prefix “nano” becomes the advertising tag.

Still another lesson we can learn deals with the contagion effects. It would be interesting to chart the occurrences to determine if there were any peaks before and after BfR’s release and the press reporting. This bandwagon effect has been observed in many different settings and tends to inflate the extensiveness of health and safety damage. Nano-cognoscenti David Rejeski and Andrew Maynard from the Woodrow Wilson Center’s Emerging Technologies project keep repeating that the reputation of the “nano” label may be at risk and “first impressions matter”.⁷ Maynard added recently, “This is a great danger—you’re going to have a response against nanotech as a whole.”⁸

Presumably, “Magic Nano is the only known, maker-identified nanotechnology product available to consumers in the form of an aerosol can”.⁹ If so, then tagging this one product as the catalyst for a contagion event is rich in potential possibilities.

This event offered a fascinating opportunity to study a product contagion event in action. The contagion is the internal operating mechanism between onset and demise of a given product line. It seldom crosses product lines and usually stays within a given company or corporation, like it did with Union Carbide and Bhopal.

When folks like Rejeski and Maynard talk about the need for regulating nanoproducts, they add a dire warning that one disaster or catastrophic event regarding a single product line might transfer to other lines and to the entire industry.

Often, this argument devolves into a retelling of the problems encountered by some companies who tried to market genetically engineered (GEMs) foods in Western Europe. Usually, the claims are associated with concerns over threats to the EC agricultural support system, damages to the European agribusiness herbicide market, and the USDA and Delta Pine & Land research on terminator seed technology. In this instance, the GEMs issue was specific to the agricultural and food industries. However, the nanotechnology industry involves very different technologies and the industry is actually a collection of many different industries from computer chip manufacturers to cosmetic companies. The crossover effect of a contagion of this nature is not known. We desperately need contagion data sets and we simply don’t have them.

⁷ A. von Bubnoff, “Study shows no nano in Magic Nano, the German product recalled for causing breathing problems,” *Small Times*, May 26, 2006, http://www.smalltimes.com/document_display.cfm?document_id=11586 (accessed June 5, 2006).

⁸ C. Piller, “Sciences’ tiny, big unknown,” *Los Angeles Times*, June 1, 2006, <http://www.latimes.com/news/printedition/front/la-fi-nano1jun01,1,3568056.story?coll=la-headlines-frontpage> (accessed June 5, 2006).

⁹ “It’s the little things that matter,” *Photonics.com*, <http://www.photonics.com/content/news/2006/April/19/82280.aspx> (accessed June 5, 2006).

Another lesson came from a colleague of mine who noticed that of the 60 German media articles on the event only 3 mentioned nanotechnology whereas all the U.S. articles mentioned the word or a term. He made this statement, “The German media focus on consumer safety, while the USA media tend to threaten the symbolic value of nanotechnology”. This is a fascinating observation and it would be interesting to better understand the intercultural dynamics at work here.

Generally, this phenomenon is unsurprising given the tendency by USA media to amplify rather than attenuate risk. Risk amplification tends to increase attention and perception and readership or viewership. Attenuation is relegated to the inside pages of a newspaper or in a retraction sidebar or ignored altogether. Fear sells and disasters and calamities sell well in the USA. Why it seems to sell better in the USA than abroad might be worth investigating, but that is best left for another day.

An additional lesson we learned is that public and private interest groups are chomping on the proverbial bit to capture as much rhetorical space in the nano-sphere as possible and for good reason. Issuing statements and press releases establish positive valence for their organization and hits on the nano-radar are ways to convince supporters to attend and contribute.

For example, it didn’t take long for the ETC Group to salivate and use the uncertain events to underline their call for a global moratorium on nanotechnology laboratory research and a recall of consumer products containing nanoparticles.¹⁰ Packaging a contemporary event as a means to add new traction to an old idea is not new. However, the decision to draw a totalistic response like a global moratorium before the causality has been established is irresponsible.

Much more cautious and contemplated remarks were offered by others. The NanoEthics Group (I am on their advisory board) categorized the incident as a wake-up call that the potential risks of nanotechnology are real and deserve more attention by both government and industry. Environmental Defense demanded spending more money on testing, plugging holes in regulation, and avoiding the use of nanoparticles in dispersive applications until more is known. The Center for Biological and Environmental Nanotechnology (CBEN)’s Kevin Ausman called for more study to learn about the toxicity values of carefully purified forms of nanoparticles. And ICON urged the regulatory authorities to complete their investigations before drawing conclusions about the health risks of other products based on the health effects of Magic Nano, and urged companies introducing products to the marketplace to engage in thorough safety reviews of their products before going to market, regardless of whether or not the products contain nanomaterials or other products of nanotechnology. These are all good ideas, but please note they were driven by the assumption that this incident was nano-related.

The final lesson learned: the German network of poison centres seem to work well and kudos belongs to BfR for raising the alert in the first place. While not trying to minimize their success, the distribution of the product was finite with one retail chain marketing the product, hence it was easily recalled. In addition, the consumers were able to correlate the breathing difficulties with the aerosol cleanser. Nonetheless, we wonder how long it would have taken for the same action-reaction process to occur in the U.S. Without a nationally linked poison reporting system, and a nearly defunct Consumer Production Safety Commission, together with

¹⁰ See <http://www.etcgroup.org/documents/NRnanoRecallfinal.pdf> (accessed May 26, 2006).

a civil liability system plagued with inefficiencies, in this country it would take a media-fed uproar and some politically savvy politician willing to champion the cause to get such a quick response.

An additional chapter to this story will be written when litigation ensues. While Magic Nano may have brought Kleinmann more business than ever, it is remarkable that we have learned so much about the event but so little about the causative agent even after a few months. Producers of nanoproducts must demand evidence of testing from upstream suppliers and would benefit from spelling that out in their contracts. It is quizzical that Kleinmann may have not. Put simply, manufacturers need to test formulations of chemical ingredients in their products under conditions of use.

Undoubtedly, aggrieved parties will turn to the courts to extract damages from Kleinmann and other responsible parties and the findings will provide an object lesson in corporate behaviour. We will learn much about the testing imbroglio when this issue resurfaces with litigation and when calls for labelling nanoproducts come to the fore.

In addition, if the allegations made by TUV Sued are true, then it behoves us to investigate how we might keep consumers informed that appropriate testing regimens have been used in testing nanoproducts. It might also be necessary to find some way to help smaller firms who do not have the means and wherewithal to conduct tests.

Once again—all opinions expressed here are the author's and do not necessarily reflect those of the National Science Foundation, the International Council on Nanotechnology, Rice University, or the University of South Carolina, neither its NanoCenter nor its NanoScience and Technology Studies group.

