Does production of the world's highest-tonnage manufactured item often involve nanotechnology?

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Introduction

Depending on the definition that one chooses to use, it can be claimed that the paper industry is the world's largest practitioner of nanotechnology. Alternatively, by using certain narrower definitions,[1] one might claim that the technology currently in widespread use by papermakers all fails to qualify as nanotechnology.

The worldwide annual production of paper products intended for printing and writing is about 104 million metric tons.[2] A large proportion of those tons, possibly more than half, are produced from fiber mixtures to which about 0.02 to 0.2% of nanoparticles have been added, on a dry-mass basis, in a sequential combination with at least one very-high-mass cationic polyelectrolyte product. Commonly used nanoparticles for such applications include colloidal silica suspensions, the primary particles of which usually are within the range of 2 to 5 nm in diameter.[3] Many of the colloidal silica products are self-assembled in such a way that they consist of fused chains of primary particles.[4] Alternatively, papermakers also can use sodium montmorillonite (bentonite) particles,[5] which have a thickness of about 0.9 nm when fully exfoliated.[6] The sequential treatment with the polyelectrolyte (usually an acrylamide copolymer or cationic starch) and nanoparticle typically results in a marked reduction of the time needed

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1 J. Harris & D. Ure, "Exploring whether 'nano-' is always necessary," *Nanotech. Percep.* **2** (2006) 173–187.

2 DeKing, N., Ed., "Global overview," in *Pulp & Paper Global Fact & Price Book*, Paperloop, Inc., San Francisco, 2004, 1–6.

3 Andersson, K. & Lindgren, E. "Important properties of colloidal silica in microparticulate systems," *Nordic Pulp Paper Res. J.* **11** (1996) 15–21, 57.

4 Iler, R. K., *The Chemistry of Silica – Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, J. Wiley & Sons, New York, 1979.

5 Langley, J. G. and Litchfield, E., "Dewatering aids for paper applications," *Proc. TAPPI 1986 Papermakers Conf.* (1986) 89–92.

6 Knudson, M. I., "Bentonite in paper: The rest of the story," *Proc. TAPPI Papermakers Conf.* (1993) 141–150.

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for water to flow from a paper sheet as it is being formed,[7] an effect that goes well beyond what can be achieved in the absence of nanoparticles.

How I have used the term

Two years ago the Pira organization (based in Leatherhead, Surrey, UK) asked me to prepare a comprehensive report on emerging technologies that are likely to affect the use of chemicals during the manufacture of paper.[8] In preparing to write that report I looked carefully at a broad range of publications dealing with nanotechnology. My criterion for considering an idea worth mentioning in the report was that the implementation step should involve the admixing of nano-objects with an aqueous suspension of cellulosic fibers. Consistent with this idea, I proposed that lottery tickets might be prepared from paper to which finely divided quantum dot material[9] had been added. The light absorbance behavior of a batch of nano-size quantum dots is unique, very hard to replicate, and a simple device could be assembled to verify that a winning lottery ticket had the correct spectrum and was not forged. I also suggested some ways in which fibers in an aqueous suspension might be treated *in situ* with self-assembled multilayers of polyelectrolytes in order to impart unique properties, such as tunable levels of hydrophobicity.

My working definition of "nanotechnology," for purposes of communication with other paper technologists, goes something like this: "Nanotechnology happens when objects having at least one dimension smaller than 10 nm are used or assembled outside the walls of a research laboratory to achieve repeatable, useful effects that cannot be achieved in the absence of the objects." Note that by this definition, the idea of adding quantum dot material during papermaking would not qualify. Probably words like "science" or "emerging technology" ought to be used in place of just "technology" when describing nascent ideas that have not yet been tested or implemented. The same thinking also would tend to exclude the concept of preparing polyelectrolyte multilayers on fibers to be used in papermaking. Although the concept has been demonstrated for purposes of increasing paper's strength,[10] there is no indication yet that the concept will be commercialized. Recent research suggests that very similar strength effects can be achieved less expensively by deposition of polyelectrolyte complexes,[11, 12] an approach that requires no changes to the equipment already being used to manufacture paper.

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[7] Hubbe, M. A. "Microparticle programs for drainage and retention," in Rodriguez, J. M., Ed., *Micro and Nanoparticles in Papermaking*, TAPPI Press, Atlanta, 2005, Chapter 1, 1–36.

[8] Hubbe, M. A., *Emerging Technologies in Wet End Chemistry*, 91 pp., Pira International, Leatherhead, UK, 2005.

[9] Brus, L. E., "On the development of bulk optical properties in small semiconductor crystallites," *J. Luminescence* **31-2** (1984) 381–384.

[10] Wågberg, L., Forsberg, S., Johansson, A., and Juntti, P., "Engineering of fiber surface properties by application of the polyelectrolyte multilayer concept. Part 1: Modification of paper strength," *J. Pulp Paper Sci.* **28** (2002) 222–228.

[11] Lofton, M. C., Moore, S. M., Hubbe, M. A., and Lee, S. Y., "Polyelectrolyte complex deposition as a mechanism of paper dry-strength development," *Tappi J.* **4** (2005, 9) 3–7.

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Narrower criteria for "nanotechnology"

The dewatering technology, as mentioned in the second paragraph of the Introduction, appears to meet the criteria of "using objects having at least one dimension smaller than 10 nm, outside the walls of a research laboratory, to achieve repeatable, useful effects that cannot be achieved in the absence of the objects." It must be admitted, however, that the definition used here strays rather far from the field of precision engineering that Norio Taniguchi[13] had in mind when he coined the term nanotechnology. As noted by Ramsden,[14] nanotechnology can be defined as deliberate placement or orderly self-assembly of objects in the nanometer range. The word "deliberate," suggesting a slow, mechanical process, seems to contrast sharply with the actuality of a state-of-the-art paper machine running at 1800 m/min. The word "orderly" seems incompatible with addition of nanoparticles to a complex mixture of fibers, minerals, polyelectrolytes, and other additives undergoing partially suppressed turbulent flow. Though precision engineering is required in the manufacture of the equipment being used to make paper, the process itself is designed to achieve a nearly isotropic mixing of all of the ingredients. The nanoparticles achieve their unique benefits, in terms of faster dewatering, by a process that leads to random locations of the nanoparticles within the sheet of paper being formed.

Let's make a final attempt to force papermakers' use of nanoparticulate dewatering aids into a narrower definition of nanotechnology,[1] which might include the words "deliberate manipulation and placement." In support of such usage, it is worth noting that the nanoparticles have no effect when added to papermaking suspensions that contain no high-mass cationic polyelectrolytes.[7] Rather, the effects depend on the presence of adsorbed polyelectrolytes on fiber surfaces. When nanoparticles are added subsequently to the mixture, they appear to (a) adsorb onto tails and loops of the adsorbed polyelectrolytes, (b) participate in the completion of polyelectrolyte bridges between different solid objects in the suspension, and (c) result in muscle-like contractions of the bridges, as polyelectrolyte segments continue to wrap themselves around the nanoparticle surfaces, due to attraction of opposite charges.[7] Adjectives that might be used to describe this self-assembly process include "repeatable," "eco-friendly," and even "highly profitable" in many of the present paper mills where the technology is employed.

Clear thinking *vs.* feeling good and making money

Although the paper industry is a major user of high technology, the fact that we make one of the lowest-cost manufactured items in the world can sometimes lead to an esteem problem. Dangle a word like "nanotechnology" in front of a bunch of paper technologists, and it can seem to us like a ticket to the high-tech club. Therefore, in the interest of clear thinking, probably it is best that papermakers avoid the use of the term nanotechnology when discussing the examples that I have listed in this essay. It is not to be assumed, however, that clear thinking is the main goal in cases where the term nanotechnology might help attract a customer or allow an idea to become a candidate for a research grant. We can only hope that educated customers and peer-reviewers will look beyond the labels and scrupulously judge the merits of each proposed idea.

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[14] Ramsden, J. "Nanotechnology in the papermaking process," *Proc. Improving Runnability for Papermakers*, Madrid, Pira International, Leatherhead, Surrey, UK, 2006, Paper 17.