MATERIALS SCIENCE AND TECHNOLOGY NEWSLETTER

Vol. 5, No. 2 SPRING-SUMMER 2008

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THE NANOSCALE REVISITED: UPDATES ON CONTACT ANGLE, SILANE ADHESION PROMOTERS AND SURFACE MODIFICATION

IN THIS ISSUE

EDITORIAL COMMENTS

With the year 2008 now more than ½ over, it is already past time to publish the Spring-Summer edition of the Newsletter. A number of items need to be covered including a short report on the just concluded CONTACT ANGLE symposium held at the University of Maine and the announcement of two upcoming symposia dealing with polymer surface modification and silane adhesion promoters. In addition, I would like to take up a recurrent theme which was covered initially in the Spring-Summer (2005) edition of the newsletter (www.mstconf.com/Vol2No1-2005.pdf) concerning the ongoing infatuation with nanotechnology in both science and industry. At that time it was pointed out that nanotechnology was in many ways a new fad that had taken hold for want of something better. Though much hype was bandied around, the core idea involved concepts whose time had finally arrived. In essence, the true substance of nanotechnology involves the fundamental understanding and manipulation of materials on the scale of roughly 10 to1000 nanometers. If one can accomplish this essential task then one can develop materials with some astounding properties that would have seemed nearly impossible only a few decades past. One upshot of this is the ability to create surperhydrophobic surfaces by manipulating the surface morphology of materials at the nanoscale as was demonstrated in a number of papers given at the recently concluded CONTACT ANGLE symposium. In fact one of the reasons CONTACT ANGLE measurements have seen such a strong revival is the fact that they are quite likely the simplest and cheapest method of probing surface interactions down to the nanoscale.

In this issue we review the current status of the nanotechnology field in regard to scientific and technical developments as well as a number of new commercial products that have finally vindicated the validity of the basic nanotechnology concept. In addition we review the past symposium on CONTACT ANGLE phenomena and present the initial announcementS of the POLYMER SURFACE MODIFICATION and SILANE ADHESION PROMOTER symposia to be held in the Summer of 2009.

NANOTECHNOLOGY REDUX: WHAT PROGRESS HAS BEEN MADE?

Commercial Products Already on the Shelf

The answer to the above question has been given quite cogently by Peter Forbes in a recent article in Scientific American[1] which I highly recommend to all readers. In a most engaging article the author documents several commercial applications of the following phenomena which result from the careful manipulation of surfaces at the nanoscale:

- SUPERHYDROPHOBICITY
- SUPERHYDROPHILICITY
- SWITCHABLE SURFACES

The applications cover a range of products and surface coatings including:

- Self cleaning paints
- Nonstainable fabrics
- Nonfoggable glass surfaces
- Self cleaning, disinfecting and deodorizing surfaces
- Switchable surfaces between hydrophilic and hydrophobic using light.

A short list of these products and the companies that produce them is given in Table 1. A quick glance at Table 1 will make it clear that the age of nanotechnology is clearly underway. Though the list is short it is nonetheless quite an impressive roll call of commercial products designed to improve the quality of life for everyone.

The Science Behind the Products

The science behind these technologies, however, got underway as early as the 1970's with the pioneering work of Wilhelm Barthlott who became enchanted with the remarkable properties of the sacred lotus leaf. Though the plant grows in muddy water in the presence of every sort of contaminant its leaves remain remarkable clean and resistant to both moisture and dirt. In addition, any water droplets which manage to remain at rest on the leaf surface tend to form near perfect spheres which sparkle remarkably in sunlight and tend to roll of at the slightest perturbation. Simple inspection of the lotus leaf does not reveal anything particularly different from any other leaf but fortunately by the 1970's scanning electron microscopes were available so Prof. Barthlott could have a very close look at the leaf surface. What was revealed was a densely packed array of waxy nodules a micron or so in size covering the entire leaf surface. The waxy material is itself hydrophobic but the array of nodules makes the surface appear superhydrophobic (contact angle greater than 150 degrees) since air gets trapped under the drop

[1] "Self-Cleaning Materials", Peter Forbes, Scientific American, August, 2008, p. 88.

between all the nodules making the drop feel as though it is suspended in air and therefore wants to take on a spherical shape. This phenomena is now fairly well known and in fact was discussed in several papers presented at the Fifth International Symposium on Contact Angle, Wettability and Adhesion Held in Toronto Canada in 2006. The topic was also discussed in detail at the Sixth Contact Angle symposium recently held at the University of Maine, Orono. More of which later. All manner of variegated surfaces can be created using photolithography and other methods all of which exhibit the superhydrophobic effect. Thus the StoLotosan™ paint listed in Table 1 uses a rough silicone surface to achieve super hydrophobicity and the NanoCare™ and NanoSphere™ fibers are treated with fine coating of hydrophobic particles which impart their non wetting and thus stain resistant properties.

TABLE 1: Short list of commercial products based on surface modification at the nanoscale

Product Name	**Function**	**Company information and website**
StoLotosan™	Self cleaning paints and finishes	UK Head Office: Sto Ltd. 2 Gordon Avenue Hillington Park Glasgow G52 4TG, UK www.stoshop.co.uk/products/detail/stolotusan-color
Nanocare™	Self cleaning nonstainable fabrics using nanofibers	Nano-Tex 2220 Livingston Street, #201 Oakland, California 94606 http://www.nano-tex.com/
Nanosphere™	Self cleaning nonstainable fabrics using nanospheres	Schoeller USA Inc. Tom Weinbender 621 Fifth Avenue North USA - Suite B Seattle WA, 98109 In Europe TASS Textilagentur Silke Glatz Ikenstrasse 47 D-40625 Düsseldorf, GERMANY http://www.schoeller-textiles.com/nanosphere/
Washlet™	Self cleaning ceramic surfaces using hydrophilic titania treatment	TOTO USA, INC. 1155 Southern Road Morrow, Georgia 30260 http://www.totousa.com
Activ Glass™	Self cleaning glass using hydrophilic titania treatment	Head Office - Pilkington United Kingdom Ltd Prescot Road Alexandra Business Park St Helens Merseyside WA10 3TT, UK http://www.pilkington.com

Moving on from superhydrophobicity, the Washlet™ and Activ Glass™ products use the opposite phenomena of superhydrophilicity to achieve roughly similar ends. In this case it is the catalytic properties of titanium dioxide (TiO_2) employed in very thin layers that gives rise to the superhydrophilic effect. Researchers in Japan discovered that by coating a suspension of TiO_2 particles on a surface and then annealing at 500 C followed by exposure to ultraviolet light, they could create a surface that was completely wettable by both water an oil. What apparently happened is that after the light exposure oxygen was removed from the surface due to the catalytic properties of TiO_2 and replaced by hydroxyl groups (-OH) making those regions highly hydrophilic. Not only that but the hydroxylated regions also formed a patchwork of nanoscale domains which gave rise to wettability

leaving the nonhydroxylated regions to account for the high wettability of oil and other nonaqueous fluids. It was clearly the nanoscale patchwork of hydrophilic and hydrophobic regions that gave rise to the unexpected dual wettability of these surfaces. Since fluids such as water will uniformly coat these surfaces they are nonfogging since no discreet droplets will form which would give rise to the high level of light scattering responsible for the fogging effect. In addition, the catalytic properties of the TiO_2 particles gave rise to further unanticipated properties such as the ability to disinfect and deodorize the treated surface. The catalytic activity of TiO_2 not only gives rise to the hydroxylated surface but also apparently attacks the cell walls of bacteria giving rise to the disinfecting and deodorizing property.

Not being satisfied with the creation of superhydrophobic and superhydrophilic surfaces, a number of researchers have thought it would be a nice idea to create surfaces that could be switched between the two modes of behavior simply by applying a light source or other electrical impulse. This phenomenon was reported on in the recent Contact Angle symposium held at the University of Maine by Pelin Chen and work is also being carried out by Kilwon Cho and collaborators in Korea. This behavior is achieved through the use of a modified azobenzene molecule which can change its conformation upon exposure to ultraviolet light. The azobenzene molecule is used to attach a hydrophobic molecule to the top of a hydrophilic polymer/silica nanoparticle layer which gives rise to a hydrophobic surface. However, upon exposure to ultraviolet light the azobenzene molecule changes its conformation which buries the hydrophobic group below the surface thus leaving a hydrophilic silica surface in its place. Removing the light source causes the azobenzene to revert to its original configuration and thus hydrophobicity reappears. At the present time no commercial products have arisen out of this type of technology but it is not difficult to imagine what could be in the offing. For instance, such surfaces would make dandy valves for micro/nano fluidic devices where all flow depends not on gravity but on surface interactions. Though it is not clear what might eventually emerge from this concept, it is clear that the technological genie is now out of the bottle and the possibilities are limited only by ones imagination.

The Gecko and the Beetle Lead the Way

As has been the case in the past, technologies that we are currently astonished to find have been old hat in the natural world for millions of years. The lotus leaf discussed above is one of the better known products of nanotechnology in the natural world. In addition, the gecko lizard has managed to hop about on vertical surfaces since prehistoric times using its nanostructured foot pads to adhere to or detach from all manner of surfaces at will. The case of the gecko was reported on in some detail in a previous issue of the newsletter (Hamaker and the Miraculous Gecko, MST Newsletter, www.mstconf.com/Vol3No1-2006.pdf , Winter -Spring, 2006). Here we look into the tricks of another nanotechnologist from natural world the Stenocara beetle which uses a clever pattern of hydrophobic and hydrophilic surfaces to gather moisture from fog in the air thus allowing it to survive in Africa's Namib costal desert where no other insect can survive. The Namib Desert lies on a thin strip of coastline forming a large section of the South-West shore of Africa. In the days of sailing ships this stretch of land was known as the infamous Skeleton Coast due to the number shipwrecks occurring there dating back to the time of the early Portugese traders who were among the first Europeans to explore this region in search of trade or treasure wherever they could find it. Many ships would find themselves victims of unpredictable storms in the South Atlantic becoming driven onto the shore. Even those who made it to land were doomed since they found themselves between the salt water of the Atlantic and a vast dry desert. Thus the skeletons refer not only to the hulks of the wrecked ships but also to the bones of the hapless sailors aboard them.

Nanoscale surfaces bring water to the desert

Curiously, the Namib Desert is not quite as dry as one might expect. Due to the large temperature difference between the water of the Atlantic and the desert sand warm moisture laden air from over the Atlantic drifts over the cooler desert at night giving rise to dense fogs which provide a large amount of moisture to those clever enough to capture it. It turns out that one local resident of the desert has developed just the right technology to capture the moisture in the fog using what a modern technologist would call a patterned nanoscale surface. The Stenocara beetle has two large wings that are covered with bumps that are mostly hydrophobic except for the very tops which are hydrophilic. The moisture in the fog is therefore attracted to the hydrophilic tops of the bumps forming droplets which grow in size till gravity pulls them off the bump and they run down into the hydrophobic valleys of the wing surface. The beetle then only needs to tilt its wings so as to drain all the collected moisture into its mouth. Thus our enterprising beetle gets all the moisture it needs from the night time fogs that regularly envelope the coast.

Apparently sometime in 2001 zoologist Andrew Parker came across the Stenocara beetle feasting on a locust which had inadvertently drifted into the desert and perished almost immediately due to the heat and lack of water. Intrigued as to how the beetle managed to survive the desert conditions where nearly every other insect would perish he uncovered the clever nanoscale pattern on the wings of the beetle and found in lab experiments using glass slides that the beetle's patterned surface is roughly twice as efficient at gathering moisture than any smooth surface regardless of whether it is hydrophobic or hydrophilic. Incited by the beetles enterprising surface technology, Dr. Parker has apparently put forward a patent to imitate the beetles process and, in partnership with the UK's defense contractor QuinetiQ, is developing it for harvesting fog on a large scale for use in arid regions such as the Namib Desert.

Thus in the realm of nanotechnology we seem to be forever playing catchup with the many natural structures that have been in operation from time immemorial. Apparently the place to learn the new nanotechnology is not the major universities or research institutes. The best instructors seem to be the unassuming life forms of the natural world such as the lotus leaf, the gecko lizard and the Stenocara beetle. However, before we can profit from the lessons taught by these creatures we need to sharpen our understanding of the nature of materials organized at the nanoscale which, as pointed out above, is the ture essence of nanotechnology.

CONTACT ANGLE, ONE OF NANOTECHNOLOGIES LEADING MEASUREMENT METHODS

As is readily apparent from a cursory reading, all of the above mentioned commercial applications of nano-engineered surfaces depends on altering and controlling the wettability of the surfaces in question. In this regard the contact angle measurement method has to be by far the most popular method for investigating this most important property. The basic reasons for this popularity may be enumerated as follows:

1. The method gives a relatively simple an intuitive indication of surface wettability.

2. With more work contact angle measurements can be used to estimate the surface free energy of a surface.

3. The contact angle drop probes only the very top outermost atomic layers of the surface under investigation thus revealing true surface properties.

4. The contact angle experiment is relatively easy to perform in a wide number of situations of both academic and commercial interest. Indeed, contact angle measurements have found an astonishing variety of applications ranging from improving the efficiency of electrical power lines to validating the authenticity of rare coins. These and other applications have been discussed in more detail in the previous issue of this Newsletter: www.mstconf.com/Vol5No1-2008

5. Equipment is widely available and relatively inexpensive from a number of vendors.

6. Several well tested formalisms exist for interpreting contact angle data.

7. Much further work remains to be done in interpreting contact angle data.

The first 6 of the above listed properties make the contact angle technique popular in applications in industry whereas the last item makes contact angle studies popular in academia. All of this explains the tremendous success of the recently completed SIXTH INTERNATIONAL SYMPOSIUM ON CONTACT ANGLE, WETTABILITY AND ADHESION held at the University of Maine, Orono the Week of July 14, 2008.

Symposium Proceedings Now Available on the MST Website

I would, therefore, like to take this opportunity to thank all of those readers of the Newsletter who participated in the symposium for making the event the success that it was and also to announce the availability of the proceedings online at the MST CONFERENCES website

www.mstconf.com/ConferenceProceedings.htm .

Posted on the website is a complete listing of every paper in the final program for the CONTACT ANGLE symposium and the accompanying symposium on PARTICLES ON SURFACES. I would like to personally thank our good friend and regular symposium participant Dr. John Durkee for suggesting that the symposium proceedings be made available in this format as it solves a number of problems we have had with past symposia in making the proceedings material available in a timely fashion. In the past all of the MST symposia have been documented in hard bound volumes which are carefully edited by the Conference Director Dr. Mittal. These volumes are of the

highest quality and represent a durable archive of every symposium going back to the inception of the series in 1998. Unfortunately a considerable amount of work is involved in producing these volumes which consumes a substantial amount of time between the close of the symposium and the time that the volumes become available. This has given rise to a number of requests from participants for preprinted material which they can access in a more timely fashion. For certain past symposia we tried making proceedings material available on a CD to those who requested it but this proved to be too time consuming for too small a number of interested participants. Making the symposium proceeding available on the website is a much more convenient and less time consuming process while making the material available to all participants who have an interest.

The symposium materials have been made public on the website according to the following rules. For those papers where the authors has given permission there is a hyperlink to one or more of the following:

1. Complete slide presentation
2. Preprint of manuscript to be published later in the symposium volume

All information is in Portable Document File (.pdf) format so as to be available to the widest possible audience.

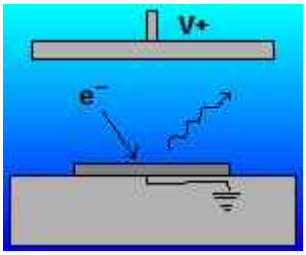
In those instances where the authors have not yet made their material available or do not want to post their material before formal publication, an E-mail address is given for the presenting author so the reader can contact that person directly for further information.

The listing is updated on a weekly basis so that authors who want to post their material but have not yet gotten around to submitting their material can do so at any convenient time. Further contributions will be posted as they are received. In addition a few authors who submitted abstracts but were unable to present their papers, due either to travel problems (late VISA application ...etc) or other personal difficulties, can still submit their papers on the website.

Any further comments, questions or helpful suggestions on this matter should be submitted to the conference chairman at the address given in the masthead of the Newsletter.

CALL FOR PAPERS: POLYMER SURFACE MODIFICATION AND SILANE ADHESION PROMOTERS

The year 2008 is now more than half over and 2009 is bearing down on us faster than one might realize. Therefore readers should be aware that two symposia dealing with polymer surface modification and silane adhesion promoters are being planned for mid July 2009. Both of these symposia are closely related to the CONTACT ANGLE symposium just completed and so many participants in that meeting should also have a strong interest in these symposia. In particular the stain resistant fiber technologies discussed above are a clear application of polymer surface modification to achieve super hydrophobic fibers. The potential applications for patterned silane surfaces is equally promising for a number innovative technologies including the already successful gene chip technology current being used in advanced genetic studies. The "Call for Papers" for each of these symposia is listed below and we invite all readers interested in submitting a paper or simply attending the symposia to submit the online registration form at the end of the Newsletter.



CALL FOR PAPERS: SEVENTH INTERNATIONAL SYMPOSIUM ON POLYMER SURFACE MODIFICATION: RELEVANCE TO ADHESION

To be held July,12-15, 2009; University of Maine, Orono, Maine, USA

This symposium continues the tradition set by the first in the series entitled: "Polymer Surface Modification: Relevance to Adhesion" which was held in Las Vegas, NV, 1993. As with its predecessors, this symposium will be concerned with the technological areas where surface modification is a key technology which allows for the processing and manufacture of products which would otherwise be unobtainable.

We are indeed happy to announce that this the 7th symposium in the series will be organized in collaboration with Prof. Douglas Gardner in the Advanced Engineered Wood Composites Center at the University of Maine, Orono, Maine. Prof. Gardner is well acquainted with problems of polymer surface modfication as applied to wood composites and is also serving on the editorial board of the Journal of Adhesion Science and Technology which is edited by the Conference Director Dr. Mittal. Prof. Gardner has been an

active researcher in the field and he and his group look forward to hosting this symposium and greeting all participants from both academia and industry from all corners of the globe.

Proper adhesion characteristics are vital to the success of any practical implementation of polymer materials. Though polymers are generally not very adhesionable, careful surface modification can result in greatly improved adhesion without altering bulk properties. This symposium is organized to bring together scientists, technologists and engineers interested in all aspects of polymer surface modification, to review and assess the current state of knowledge, to provide a forum for exchange and cross-fertilization of ideas, and to define problem areas which need intensified efforts.

The invited speakers have been selected so as to represent widely differing disciplines and interests, and they hail from academic, governmental and industrial research laboratories. This meeting is planned to be a truly international event both in geographic coverage as well as in spirit.

AMONG TOPICS TO BE COVERED ARE:

SURFACE MODIFICATION TECHNIQUES

- Plasma, ultraviolet, corona, laser, ion beam, flame ...
- Mechanical roughening
- Monolayer deposition, grafting and wet chemical

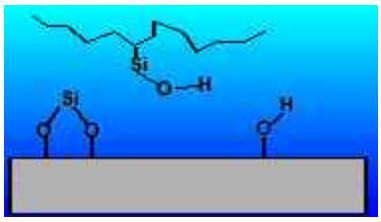
POLYMER SURFACE MODIFICATION FOR ADHESION IMPROVEMENT OF:

- Metal layers (metallized plastics)
- Organic coatings, inks, composites, adhesive joints, microorganisms

APPLICATIONS AND SURFACE CHARACTERIZATION

- Packaging, composites, biological implants
- Microelectronics, aerospace, marine...
- All methods for characterization of surface chemistry and morphology, (CONTACT ANGLE, ESCA, SIMS, AFM ...)

CALL FOR PAPERS
SEVENTH INTERNATIONAL SYMPOSIUM ON
SILANES AND OTHER COUPLING AGENTS
To be held July 15-18, 2009; University of Maine, Orono, Maine, USA



This symposium continues the tradition set by the first symposium in this series:"Silanes and Other Coupling Agents" which was hosted in 1991 by the Dow Corning Corporation in honor of Dr. Edwin P. Plueddemann. As with its predecessors, this symposium will be concerned with the technological areas where the use of surface primers such as silanes is critical to the success of many technologies.

We are indeed happy to announce that this the 7th symposium in the series will be organized in collaboration with Prof. Douglas Gardner in the Advanced Engineered Wood Composites Center at the University of Maine, Orono, Maine. Prof. Gardner is well acquainted with problems of adhesion and coupling agents as applied to wood composites and is also serving on the editorial board of the Journal of Adhesion Science and Technology which is edited by the Conference Director Dr. Mittal. Prof. Gardner and his group look forward to hosting this symposium and greeting all participants from both academia and industry from all corners of the globe.

Historically the silanes have been used as coupling agents for thin films in the microelectronics industry and in glass fiber composites where the use of silanes has been an enabling factor in the success of many manufactured products. Quite surprisingly, silanes have also found a role in biotechnology as specific coupling agents for bonding polynucleotides to the so-called "gene chips" , in corrosion protection of metals and also as stabilizing coupling agents in cosmetic formulations. This symposium is organized to bring together scientists, technologists and engineers interested in all aspects of coupling agent technology, to review and assess the current state of knowledge, to provide a forum for exchange and cross-fertilization of ideas and to define problem areas which need intensified efforts. The invited speakers have been selected so as to represent widely differing disciplines and interests, and they hail from academic, governmental and industrial research laboratories. This meeting is planned to be a truly international event with participation from academic and industrial institutions worldwide.

AMONG TOPICS TO BE COVERED ARE:

- Mechanisms of silanes action.
- Role of silanes in adhesion of coatings, composites and adhesive joints.
- Deposition techniques:

  - solution
  - plasma
  - vapor
  - electrochemical

- Non-silane adhesion promoters.
- Plasma polymerized coatings as adhesion promoters.
- Relevance of silanes in durability of bonds.
- Applications:

  - coatings, corrosion inhibitors
  - adhesive joints, composites
  - biological applications, cosmetics

- Silane surface characterization.

  - Standard: contact angle, FTIR,...
  - Advanced: neutron scattering, ...

Submitting a Paper

These symposia are being organized by MST Conferences, LLC under the direction of Dr. K. L. Mittal, Editor, Journal of Adhesion Science and Technology(JAST) and in collaboration with Prof. Douglass Gardner at the University of Maine. It is planned to document these symposia in the Journal of Adhesion Science and Technology. Please notify the conference chairman of your intentions to present a paper as early as possible. An abstract of about 200 words should be sent by **January 15, 2009** to the conference chairman by any of the following methods:

E-mail: rhl@mstconf.com
FAX: 212-656-1016
Regular mail:

Dr. Robert H. Lacombe
Conference Chairman
3 Hammer Drive
Hopewell Junction, NY 12533

Contact by phone: 845-897-1654; 845-227-7026
Full conference details and registration via the Internet will be maintained on our web site. Click on either of the hyperlinks below to submit an abstract for the conference or to get on the registration list to receive ongoing updates concerning the symposia:

For **POLYMER SURFACE MODIFICATION**

http://mstconf.com/surfmod7.htm

For **SILANE ADHESION PROMOTERS**

http://mstconf.com/silanes7.htm