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CONTACT ANGLES: A SURPRISINGLY UBIQUITOUS PHENOMENON

EDITORIAL COMMENTS

Just when you thought you had explored all the applications of contact angle phenomena, yet another comes from seemingly nowhere. In this regard, recent work from MIT reveals a remarkable application of the superhydrophobic effect which has potentially enormous consequences for the power industry. Details of this breakthrough are the subject of this issues editorial essay. This development comes at a very opportune moment as we also want to announce the upcoming 9th international symposium on Contact Angle, Wettability and Adhesion to be held at Lehigh University the week of June 16, 2014.

In addition we review two new volumes dealing with surface wetting which also dovetails very nicely with the contact angle symposium. Finally we would like to announce an upcoming meeting on thin films which is another topic closely related to surface energetics and wetting behavior.

CONTACT ANGLE: THE PHENOMENON WITH NEAR ENDLESS APPLICATIONS

Our colleague Carl Clegg of the Ramé-Hart company published a list of more than 50 applications of contact angle behavior in his periodic newsletter:

http://www.ramehart.com/newsletters/2010-12_news.htm

If this was not enough Carl went on to describe 6 more applications in his March 2010 issue:

http://www.ramehart.com/newsletters/2010-03_news.htm

This issue added 6 further applications including wind, solar, nuclear power, electric cars, biofuels and carbon capture. This brings the total to 56 applications but I doubt we are anywhere near the end of the list since contact angle phenomena are intimately affected by surface interactions and surfaces are everywhere and affect nearly everything.

One of the latest developments concerns the behavior of charged droplets near superhydrophobic surfaces. This has been documented in the literature in the following paper from Prof. Evelyn Wang's group at MIT:

Electrostatic Charging of Jumping Droplets; Nenad Miljkovic, Daniel J. Preston, Ryan Enright and Evelyn N. Wang, *Nature Communications*, 4, 2517 (2013) (doi:10.1038/ncomms3517)

The MIT researchers discovered that tiny water droplets that form on a superhydrophobic surface, and then jump away from that surface, carry an electric charge. At first glance this seems more like some sort of academic curiosity as opposed to a technical breakthrough, but the finding could lead to more efficient power plants and a new way of drawing power from the atmosphere.

Previous work showed that under certain conditions droplets can actually leap away from a surface , rather than simply sliding down and running off due to gravity. This behavior occurs when water condenses onto a specific kind of superhydrophobic surface forming droplets at least two of which coalesce. The droplets subsequently jump from the surface due to apparent opposing charges with the concomitant release of excess energy.

Using high speed video equipment the researches saw that the jumping droplets repel one another in midflight and are also attracted toward an electrically charged wire demonstrating that they carry an electric charge. In order to understand the reason for the repulsion between jumping droplets after they leave the surface, the researchers performed a series of experiments using a charged electrode. When the electrode had a positive charge, droplets were repelled by it as well as by each other; when it had a negative charge, the droplets were drawn toward it. This established that the effect was caused by a net positive electrical charge forming on the droplets as they jumped away from the surface. The actual charging process is quite likely the same charge stripping mechanism which occurs routinely in the atmosphere as warm moist air rises. This is the phenomenon which gives to the enormous potential differences between the top of thunder clouds and the earth's surface which is the driving force for lightning strikes.

From a practical viewpoint this work opens the door to a technology which could greatly increase the efficiency of steam condensers which are a key element in nearly every power plant on the planet. Nearly all conventional power plants generate electricity by creating high pressure steam from some energy source or another. The steam is directed onto a turbine causing it to spin rapidly and thereby generate electricity by driving a generator. The exiting low pressure steam goes to a condenser which turns it back to water so the whole process can repeat indefinitely. The lowly condenser is a rather dull but nonetheless key component in the overall process and its efficiency affects the overall efficiency of the power generation process. The condenser is attached to the exhaust end of the turbines which drive the generators. One of the tasks of the condenser is to keep the pressure at its end of the turbine lower than the pressure at the boiler end, meaning a greater flow rate through the blades causing the turbine spin faster and thus generate more power for a given energy input from the energy source such as coal, oil, gas or nuclear fuel. Thus one can envisage applying a suitable hydrophobic coating to the surface of a condenser and also applying a suitable electric field to attract the charged droplets which are formed. This can greatly increase the efficiency of the condensation process. Rather than let the condensed moisture form a film which runs off upon attaining a large enough thickness, the moisture is condensed right away into small droplets which are quickly carried away by an electric field. This new process can give rise to a projected increase in overall generation efficiency of roughly 10%. Thus the potential impact on power generation is enormous.

BOOK REVIEWS

Wetting of Real Surfaces, By Edward Yu. Bormashenko, (Walter de Gruyter GmbH, Berlin/Boston, 2013)

This volume arrived in our office at an opportune moment given that we are now preparing for the ninth in the ongoing series of symposia dealing with Contact Angle, Wettability and Adhesion of which more will be said at the end of the newsletter. In this rather compact monograph Prof. Bormashenko provides a rather comprehensive account of the theoretical developments in the field of contact angle and wettability of surfaces.

Interestingly, Prof. Bormashenko points out that the field of contact angle and wettability remained rather a backwater endeavor in the field of modern physics from the time of Thomas Young's pioneering work up to roughly the 1990's despite the fact that Einstein, Schrödinger and Bohr devoted a significant portion of their research activity to this topic. Much of this stems from the fact that surfaces presented a rather messy and intractable research topic due to the difficulty in obtaining well defined surfaces free of contamination and other defects. Indeed the eminent theoretical physicist Wolfgang Pauli remarked that "God created matter but the Devil created surfaces". Thus the solid state physics literature up to about the early 1980's tended to be dominated by topics such as superconductivity, electronic band structure, phase transitions, semiconductors and similar topics dealing with the bulk behavior of solids.

This all started to change significantly by about the 1980's being led in large part by the microelectronics industry which was fabricating multilevel thin film structures which were becoming more and more dominated by interfacial surfaces between metals, insulators and semiconductors. Even by the early 1970's it was becoming apparent that in order to fabricate devices with higher and higher circuit densities it was critical to understand the nature of the interactions between the various material components at their contact surfaces. This need was supported by advances in microscopy starting with electron microscopy and evolving further to electron tunneling microscopy and finally to the now ubiquitous atomic force microscopy. On top of this a number of surface analysis techniques emerged nearly too numerous to mention the most popular of which being X-ray Photoelectron Spectroscopy (XPS also called ESCA Electron Spectroscopy for Chemical Analysis).

The need for understanding surface properties was of course not limited to the microelectronics industry. The entire coatings industry needed to understand the wetting properties of various paints and inks and the biotechnology industry dealing with medical implants needed to understand how the surfaces of their devices would interact in the in vivo environment. The contact angle technique thus started to emerge as a low cost and highly sensitive method for exploring the wetting behavior of surfaces.

A critical juncture of sorts was achieved with the work of Barthlott and Neinhuis in 1997[1] who first studied the extreme hydrophobicity of the lotus leaf and its effect in removing all manner detritus from the leaf's surface. This work lead to a literal explosion of work on the superhydrophobic effect with is apparent application to self cleaning surfaces and other highly innovative applications.

Getting back to Prof. Bormashenko's volume a brief look at the table of contents reveals a rather wide range of topics:

[1] "Purity of thr Sacred Lotus or Escape from Contamination in Biological Surfaces", W. Barthlott and C. Neinhuis, *Planta*, 202, 1 (1997).

6. Superhydrophobicity, superhydrophilicity and the rose petal effect

7. Wetting transitions on rough surfaces

8. Electrowetting and wetting in the presence of external fields

9. Nonstick droplets

There is clearly not enough space here to cover all of the above topics in any detail so we will focus on chapter 6 dealing with super hydrophobic and hydrophilic phenomena which, as Prof. Bormashenko points out, are among the currently most actively researched topics in the contact angle field.

Interestingly, the author points out that exhibiting a high contact angle is not sufficient to define a state of superhydrophobicity as might casually be assumed. In addition the contacting water drop must also exhibit low contact angle hysteresis. That is the advancing and receding contact angles must be approximately the same. This property is required for the so called "lotus leaf" effect where water drops not only form with a high contact angle but also roll very easily off the leaf carrying any collected debris with them as shown in figure 1.

The counter example is the "rose petal" effect reported on by Jiang and co-workers.[2] These investigators looked at water droplets on rose petals which also form very high contact angles but unlike the lotus leaf case these drops also exhibit a very strong hysteresis. An immediate consequence is that these drops do not roll even when held at a steep angle as also shown in figure 1.

A further subtle point brought out in the chapter is the fact that the substrate material does not have to be highly hydrophobic in order to exhibit the superhydrophobic effect. The lotus leaf material is in fact hydrophilic. What gives rise to the superhydrophobic behavior is the *hierarchical relief morphology* of the surface. An example of such a structure would be the fractal Koch curve shown schematically in figure 2. The author goes on to analyze the wetting of these highly variegated surfaces in terms of the Wenzel and Cassie models covered in chapter 5.

In all this volume can be highly recommended to anyone interested in coming up to date on the latest theoretical developments in the rapidly expanding field of contact angle phenomena.

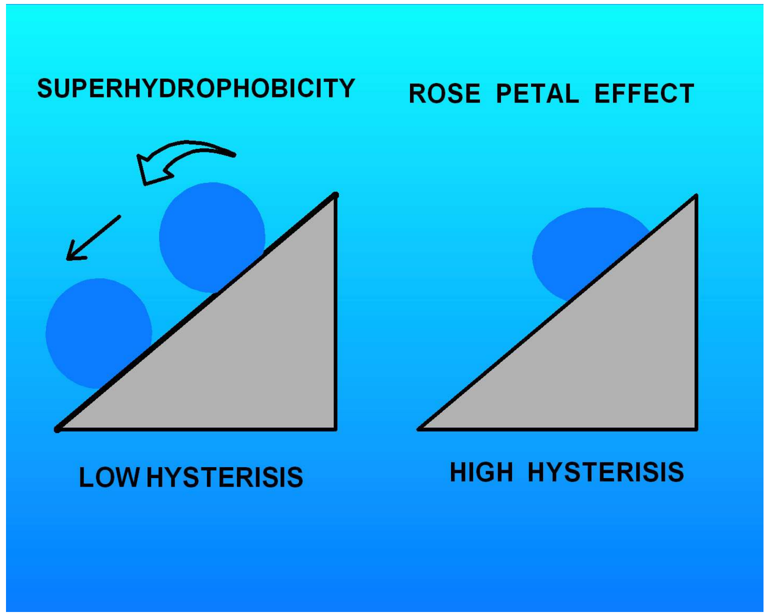

Figure 1 Schematic illustrating the difference between a truly superhydrophobic surface and one exhibiting only a high contact angle

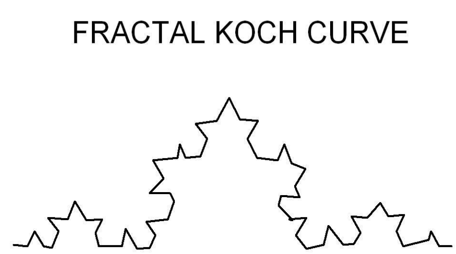

Figure 2 Example of a hierarchical relief morphology.

ADVANCES IN CONTACT ANGLE, WETTABILITY AND ADHESION: VOLUME 1; Edited by K. L. Mittal, Wiley Scrivener Publishing (2013)

This book starts a new series of edited volumes intended to document the ever expanding field of contact angle and wettability phenomena. Unlike Prof. Bormashenko's narrowly focused monograph reviewed above this volume covers nearly the entire range of research activity going on world wide ranging from highly mathematical modeling work using finite element methods to highly applied studies of the use of contact angle measurements in the wood products industry. Again the range of

[2] "Petal effect: A superhydrophobic state with high adhesive force", L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia and L. Jiang, *Langmuir*, 24, 4114 (2008).

topics covered is best illustrated by listing the table of contents:

Part 1: Fundamental Aspects

1. Correlation between ontact Line Pinning and Contact Angle Hysterisis on Heterogeneous Surfaces: A Review and Discussion; Mohammad Amin Sarshar, Wei Xu and Chang-Hwan Choi

2. Computational and Experimental Study of Contact Angle Hysterisis in Multiphase Systems; Vahid Mortazavi, Vahid Hejazi, Rosan M D'Souza and Michael Nosonovsky

3. Heterogeneous Nucleation on a Completely Wettable Substrate; Masao Iwamatsu

4. Local Wetting at Contact Line on Texture Hydrophobic Surfaces; Ti Li and Yanguang Shan

5. Fundamental Understanding of Drops Wettability Behavior Theoretically and Experimentally; Hartmann E. N'guessan, Robert White, Aisha Leh, Arnab Baksi and Rafael Tadmor

6. Hierarchical Structures Obtained by Breath Figures Self-Assembly and Chemical Etching and their Wetting Properties; Edward Bormashenko, Sagi Balter, Roman Grynyov and Doron Aurbach

7. Computational Aspects of Self-Cleaning Surface Mechanisms; Muhammad Osman, Raheel Rasool and Roger A. Sauer

8. Study of Material-Water Interactions Using the Wilhelmy Plate Method; Eric Tomasetti, Sylvie Derclaye, Mary-Hélène Delvaux and Paul G. Roushet

9. On the Utility of Imaginary Contact Angles in the Characterization of Wettability of Rough Medicinal Hydrophilic Titanium; S. Lüers, C. Seitz, M. Laub and H. P. Jennissen

10. Determination of Surface Free Energy at the Nanoscale via Atomic Force Microscopy without Altering the Original Morphology; L. Mazzola and A. Galderisi

Part 2: Superhydrophobic Surfaces

11. Assessment Criteria for Superhydrophobic Surfaces with Stochastic Roughness; Angela Duparré and Luisa Coriand

12. Nanostructured Lubricated Silver Flake/Polymer Composites Exhibiting Robust Superhydrophobicity; Ilker S. Bayer, Luigi Martiradonna and Athanassia Athanassiou

13. Local Wetting Modification on Carnauba Wax-Coated Hierarchical Surfaces by Infrared Laser Treatment; Athanasios Milionis, Roberta Ruffilli, Ilker S. Bayer, Lorenzo Dominici, Despina Fragouli and Athanassia Athanassiou

Part 3: Wettability Modification

14. Cold Radiofrequency Plasma Treatment Modifies Wettability and Germination Rate of Plant Seeds; Eduard Bormashenko, Roman Grynyov, Yelena Bormashenko and Elyashiv Drori

15. Controlling the Wettability of Acrylate Coatings with Photo-Induced Microfolding; Thomas Bahners, Luta Prager and Jochen S. Gutmann

16. Influence of Surface Densification of Wood on its Dynamic Wettability and Surface Free Energy; M. Petrič, A. Kutnar, L. Rautkari, K. Laine and M. Hughes

17. Contact Angle on Two Canadian Woods: Influence of Moisture Content and Plane of Section; Fabio Tomczak and Bernard Riedl

18. Plasma Deposition of ZnO Thin film on Sugar Maple: The Effect on Contact Angle; Fabio Tomczak, Bernard Riedl and Pierre Blanchet

19. Effect of Relative Humidity on contact Angle and its Hysterisis on Phospholipid DPPC Bilayer Deposited on Glass; Emil Chibowski, Konrad Terpilowski and Lucyna Holysz

Part 4: Wettability and Surface Free Energy

20. Contact Angles and Surface Free Energy of Solids: Relevance and Limitations; Paul G. Rouxhet

21. Surface Free Energy and Wettability of Different Oil and Gas Reservoir Rocks; Andrei S. Zelenev and Nathan Lett

22. Influence of Surface Free Energy and Wettability on Friction Coefficient between Tire and Road Surface in Wet Conditions; L. Mazzola, A. Galderisi, G. Fortunato, V. Ciaravola and M. Giustiniano

Again there is far more material in this volume than can be commented upon in the limited space available here so I will only comment on the highly original and innovative paper by Jennissen and coworkers dealing with "The Utility of Imaginary Contact Angles in the Characterization of Wettability of Rough Medicinal Hydrophilic Titanium".

The classic Young's equation deriving from the seminal work of Thomas Young ("An Essay on the Cohesion of Fluids", Phil. Trans. Roy. Soc., 95, 65 (1805)) but curiously not written down in that paper, is given by:

$$\cos(\theta) = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \qquad (1)$$

This venerable icon of contact angle theory has been used for at least the last 50 years to analyze contact angle data of various liquids on polymers and other low energy surfaces. In this case the right hand side of Eq. 1 is less than 1 And so the cosine function is well defined at least in a conventional sense. What happens, however, when a drop of liquid is applied to a high surface energy metal. Then γ_s can be quite a bit larger than γ_{sl} and the right hand side of Eq. 1 can be greater than 1. Check just about any standard math table of trigonometric functions and you have to conclude that the cosine function is never larger than 1 which implies that Eq. 1 is likely not applicable in the case of certain liquid/metal combinations? Not to despair , however. Any mathematician will tell you that the cosine is a perfectly analytical function defined over the entire complex plane. The inverse cosine function for arguments greater than 1 thus show up in the complex plane. I happen to use a fairly sophisticated math analysis program and if I ask it what is the angle whose cosine is 1.5 it gives the answer 0.9624i, where $i = (-1)^{½}$ which is a purely imaginary number. Imaginary numbers are certainly nothing new and have been in routine use in the analysis of electrical and mechanical vibrating systems and in the analysis of wave phenomena in general. What is new in this paper is that Jennissen and coworkers have demonstrated that imaginary numbers have utility in the description of the wetting of high energy metal surfaces.

So what is going on. For a liquid spreading on a high energy metal surface the wetting is so complete that there is no measurable contact angle. Thus a standard contact angle goiniometer is of no use in trying to measure the wetting behavior. However, other surface energy measurement tools are available such as the Wilhelmy Plate technique. By this method a thin plate of the substrate material suspended from a sensitive strain gage is dipped into a reservoir of the test liquid[3]. The resulting surface tension induced by the spreading liquid is measured through the strain gage and by this method a value of the contact angle can be inferred. Since what is measured is essentially a surface energy there is no problem analyzing high surface energy metals such as the highly hydrophilic titanium studied in this paper. It is not clear whether or not this method will come into wide use in the field of surface analysis but there is certainly no physical or mathematical reason why it should not. The interested reader can consult the paper for full details.

UPCOMING MEETINGS AND SHORT COURSES

THINFILMS2014 ; 15 th - 18 th July 2014, Chongqing, China

All who have an interest in thin film technology and its many applications will definitely want to look into this meeting organized by Thin Films Society and Chongqing University

Important Deadlines:

Abstract submission: 15 th March 2014
Notice of Acceptance: 31 st March 2014
Full manuscript: 20 th July 2014
Early Bird Registration: 31 st May 2014

Web site:

www.thinfilms-Singapore.org
www3.ntu.edu.sg/thinfilms/thinfilms/

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[3] For details on the Wilhelmy plate method see "Physical Chemistry of Surfaces", Arthur W. Adamson and Alice P. Gast, (Wiley Interscience, 1979)

Symposia & Symposium Chairs:

1. Biological coatings (Kui CHENG & Jan CIZEK)
2. Coatings for clean energy (Joe HSIEH & Lidong SUN)
3. Coatings towards industrial applications (Yanwen ZHOU & Peter KELLY)
4. Electrochemistry of thin films (Erjia LIU & San Ping JIANG)
5. Functional ceramic thin films (Pei - Chen SU & Wonyoung LEE)
6. Mechanical properties of thin Films (Zhong CHEN & Vicky CHEN)
7. Nanostructured and nanocomposite films and coatings (Sam ZHANG & Jyh - Ming TING)
8. Optoelectronic & dielectric thin films (Guenther BENSTETTER & Dongping LIU)
9. Oxide thin film, nano - and heterostructures (Gregory GOH & Sanjay MATHUR)
10. Organic/polymer thin films (Lin LI & Masayuki YAMAGUCHI)
11. Photocatalysis and self - cleaning coatings (Guojun QI)
12. Smart materials and films (Richard FU & Yan LI)

Ninth International Symposium on
CONTACT ANGLE, WETTABILITY AND ADHESION
Rauch Business Center
Lehigh University
Bethlehem Pennsylvania
June 16-18, 2014

SYMPOSIUM HISTORY AND MOTIVIATION

In his opening remarks at the first symposium in this series Professor Robert Good pointed out that Galileo in the 17th century was quite likely the first investigator to observe contact angle behavior with his experiment of floating a thin gold leaf on top of a water surface. Since that time contact angle measurements have found wide application as a method for determining the energetics of surfaces. This, in turn, has a profound effect on the wettability and adhesion of liquids and coatings to surfaces.

This symposium will be concerned with both the fundamental and applied aspects of contact angle measurements. Issues such as the applicability and validity of various measurement techniques and the proper theoretical framework for the analysis of contact angle data will be of prime concern.

In addition, a host of applications of the contact angle technique will be explored including but not limited to: wettability of powders, fibers, wood products, paper, polymers and monolayers. Further focus will be on the use of contact angle data in evaluating surface modification procedures, determining relevance of wettability to adhesion, the role of wettability in bioadhesion, ophthalmology, prosthesis and in the control of dust in mining and milling applications.

AUDIENCE AND PARTICIPATION

The primary focus of this symposium will be to provide a forum for the discussion of cutting edge advancements in the field and to review and consolidate the accomplishments which have been achieved thus far.

SUBMITTING A PAPER

This symposium is being organized under the direction of Dr. K. L. Mittal, Editor Reviews of Adhesion and Adhesives and by MST Conferences. 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 February 15, 2014 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:

www.mstconf.com/Contact9.htm

To get on the mailing list to receive ongoing details concerning the symposium please submit the response form at:

www.mstconf.com/resp-sprg-2014.htm

3- Day Impact Course
The Chemistry, Physics & Mechanics of Adhesion Science

April 23-25, 2014
Courtyard by Marriott, Stewart-Newburgh, NY
SCENIC HUDSON VALLEY

Adhesion's Important Role Today

Adhesion plays an important role in many technologies and industries, viz., aerospace, microelectronics, automotive, thin films, optics, coatings, paint and so on. Broadly speaking, the topic can be divided into two categories: film or coating/substrate combination, and adhesive joint. Films and coatings are used for a variety of purposes and irrespective of their intended function, these must adhere adequately to the underlying substrate. So the need for understanding and controlling the factors affecting adhesion is quite patent.

Furthermore, the durability of the bond (on exposure to process chemicals, moisture, corrosives, etc.) is of grave concern and importance. This course presents an overview of the chemistry, physics and mechanics of adhesion in regard to understanding fundamental adhesion mechanisms. You will learn how to improve and control them and the latest adhesion measurement techniques which are being used to evaluate the PRACTICAL ADHESION of coatings and laminate structures.

Emphasis is given to methods which can be carried out in a manufacturing environment as well as in the lab environment; which give results that are directly relevant to the durability and performance of the structures under investigation. The effects of coating elastic properties and residual stress are considered as well as other external influences which affect durability under use conditions.

Topics to be Covered

I. Surface Contamination and Cleaning
II. Theories or Mechanisms of Adhesion
III. Contact Angle, Wettability and Adhesion
IV. Investigation of Interfacial Interactions
V. Surface Modification Techniques including Plasma
VI. Ways to improve Adhesion of Organic Coatings
VII. Silanes and Other Adhesion Promoters
VIII. Adhesion Aspects of Thin Films
IX. Adhesion Measurement of Films and Coatings
X. Basics of Adhesion Measurement
XI. Residual Stress and Material Mechanical Properties
XII. Setting Adhesion Requirements for Coating Applications
XIII. Adhesion Measurement at Atomic and Molecular Level
XIV. Applications to real world problems of product development and manufacturing

How You Will Benefit From This Course

You will understand advantages and disadvantages of a range of adhesion measurement techniques. You will be able to select the right surface cleaning technique including the use of atmospheric plasma. You will utilize the concept of acid-base interactions in improving adhesion, acquire basic skills for addressing adhesion failure problems, analyze the alternatives and select the optimum technique for improving adhesion, and durability. Know where help is available in emergency situations and learn how to select the best measurement technique for a given application.

Audience: Scientists and professional staff in R&D, manufacturing, processing, quality control/reliability involved with adhesion aspects of coatings and adhesion sensitive applications.

Level: Beginner- Intermediate; introduction/overview

Prerequisites: Elementary background In chemistry, physics or materials science.

Duration: 3 days

Course fee and materials: $1,295, includes break refreshments, complete set of lecture notes and copy of handbook and reference guide ADHESION MEASUREMENT METHODS: THEORY AND PRACTICE, (CRC PRESS, 2006)

Further details concerning the short course are maintained on the conference web site at:

www.mstconf.com/AdhesionCourse.htm

To get on the mailing list to receive ongoing updates concerning the short course please submit the response form at:

www.mstconf.com/resp-sprg-2014.htm