## November 14, 2010 Expert Witness Report

Report and Opinion Re: David Stiggers v P&G and Hunt

This report incorporates information obtained from a site visit to the F&HCIC Annex on August 26, 2008 as well as a follow-up inspection on November 7, 2008, and a review of relevant literature and patents as well as depositions, photographs and materials available in the case record. A list of the materials that were consulted is included in Appendix A.

## **Summary of Professional Experience:**

I have been a Professor of Chemical and Materials Engineering at the University of Cincinnati for 16 years with a PhD in Polymer Science and Engineering from the University of Massachusetts, Amherst and a B.S. in Chemical Engineering from the University of Rhode Island as well as a B.S. in Zoology. I have also worked in the chemical industry (Pfizer and Hoechst) and as a Patent Examiner. I conducted post-doctoral research at Sandia National Laboratory in Albuquerque New Mexico for several years prior to my current position. I am a member of the American Chemical Society, American Institute of Chemical Engineers, and the American Physical Society in which I am a fellow. I am on several advisory boards for Argonne National Laboratory and Oak Ridge National Laboratory and frequently serve as a referee for the Department of Energy, Department of Commerce and the National Science Foundation as well as for a number of Journals. I have approximately 120 peer-reviewed papers in the scientific literature and have an H-index of 27. I present approximately 7 invited talks per year on a variety of technical subjects pertaining to my research. I teach approximately 5 courses per year at the undergraduate and graduate levels in a variety of subjects pertaining to Materials Science and Chemical Engineering. For this report, I rely on broad exposure and expertise in the chemical industry. I have previously worked with Freking & Betz LLC in technical consulting on cases pertaining to the chemical industry. A brief CV is attached to this report as Appendix B.

For the David Stiggers v P&G and Hunt case, I was retained as an expert witness to assist with the determination of the likely cause of the explosion that occurred on June 13, 2008. The opinions presented in this report are given to a reasonable degree of scientific probability and certainty.

# **Report and Assessment:**

On Friday June 13, 2008 an explosion occurred at the Procter & Gamble facility Fabric and Home Care Innovation Center (F&HCIC Annex) at 5299 Spring Grove Avenue in Ivorydale (Cincinnati OH, 45217) injuring David Stiggers who was a construction worker removing waste lines from the site. The explosion occurred when Mr. Stiggers attempted to cut a waste pipe in the ceiling of the first floor of the F&HCIC Annex below a floor drain on the second floor using a handheld band saw. An inspection was conducted on August 26, 2008 as well as a follow-up inspection on November 7, 2008.

The apparent cause of the explosion was a combination of the benzoyl peroxide deposited

in the drain pipe as well as blockage of the drain pipe at the floor level (on the level above the accident site) and downstream from the benzoyl peroxide deposit that effectively sealed the benzoyl peroxide in the drain pipe. After the explosion approximately 100 grams of benzoyl peroxide visibly remained in the pipe. Some of this was sampled and analyzed by a lab (Chemir Analytic Services) under contract to Procter & Gamble. Benzoyl peroxide spontaneously degrades at approximately 60° C (140 °F) and can explosively degrade when exposed to a spark. The rapid degradation forms first benzoic acid then phenyl radical and two moles of  $CO_2$  for every mole of benzoyl peroxide. The products are not acutely toxic but the rapid release of  $CO_2$  gas as well as the associated heat of degradation lead to a self-accelerating explosion. In the F&HCIC Annex explosion, the pipe was heated by the band saw or a spark from the saw led to ignition of the deposited benzoyl peroxide. The pipe blockage caused the pipe to explode due to the rapidly released  $CO_2$ . The explosion of benzoyl peroxide results in a white cloud of benzoic acid and phenyl radicals as was observed by David Stiggers and others at the scene of the explosion.

Dangers associated with explosions of benzoyl peroxide are well known in industrial settings. Five years prior to the Ivorydale explosion a parallel industrial accident occurred at a U.S. Chemical & Plastics, Inc. facility in Gnadenhutten, Ohio. This explosion received attention in the press and the U.S. Secretary of Labor Elaine L. Chao was quoted as saying "It was fortunate that this explosion occurred during the lunch hour, or workers very well may have lost their lives..."

Benzoyl peroxide has three primary industrial uses. It is used as a free radical initiator for polymerizations such as in the synthesis of polystyrene (for example Styrofoam<sup>®</sup>). In this process, use is made of the phenyl radical degradation product. The U.S. Chemical & Plastics plant, mentioned above, was producing benzoyl peroxide for use in the plastics industry. Benzoyl peroxide is also used as bleach and as an antiseptic, particularly in the treatment of acne. Benzoyl peroxide is used in a number of consumer products as a bleach such as in toothpaste, and hair dye. It is used in dishwasher detergents because it can remove tomato stains from plastic dishes. Two inherent problems with some of these applications are the insolubility of benzoyl peroxide in water and the low shelf-life of benzoyl peroxide due to its reactivity. Benzoyl peroxide degrades rapidly in alkaline conditions. Many detergent compositions are alkaline leading to a third problem with the use of benzoyl peroxide as a bleach in detergents.

Benzoyl peroxide is used in several P&G products such as Cascade Plastic Booster<sup>®</sup>, which is a paste product used in conjunction with dishwashing detergents whose active ingredient is benzoyl peroxide. Cascade Plastic Booster<sup>®</sup> and other benzoyl peroxide/detergent systems were probably developed at the F&HCIC Annex in the 1990's since the patent record (U. S. Patents 5,663,113, 5,710,115, 5,763,378, 5,904,161, 6,306,219 and 6,440,920) all have initial filing dates (or PCT filing dates) from December, 1994 to July, 1997. Generally the product development stage predates the filing date by at least one year. After 1997 no further patents pertaining to benzoyl peroxide seem to originate at F&HCIC though Procter & Gamble has only provided information on activities at F&HCIC after 1999. The aim of the Procter & Gamble patents in this area seek to extend the shelf-life of benzoyl peroxide in detergent products, to protect benzoyl peroxide from the inherently alkaline conditions of detergents and to increase the effective reactivity of benzoyl peroxide to certain types of stains by reduction in the size of benzoyl peroxide particles (thereby increasing the surface area). Cascade Plastic Booster<sup>®</sup>

was discontinued as a Procter & Gamble product 10 months after the F&HCIC explosion in April of 2009.

Benzoyl peroxide is not soluble in water. The MSDS suggested disposal route for small amounts of untreated benzoyl peroxide is to react it with an alkaline solution of NaOH in a 10% water solution (making perbenzoic acid) and to flush it down the drain since the decomposition products are not acutely toxic. Disposal of the larger quantities encountered in an industrial setting involve the following process according to a producer of benzoyl peroxide (Mallinckrodt Chemicals, Phillipsburg, NJ): "Whatever cannot be saved for recovery or recycling should be handled as hazardous waste and sent to a RCRA approved waste facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations." Benzoyl peroxide is considered a highly reactive/explosive chemical waste.

The modification of benzoyl peroxide in the patented Procter & Gamble compositions and methods would render the disposal method for benzoyl peroxide in the MSDS (treatment with an alkaline solution and flushing down the drain) inappropriate and, in fact, dangerous. The extended shelf-life, small particles size and protection from alkaline and aqueous solutions are ideal conditions for the formation of benzoyl peroxide deposits in drain pipes. This should have been obvious to those familiar with chemical safety. The extent of deposits of treated benzoyl peroxide in the drain pipe and the lifetime for these treated deposits is not known without further testing since the treated benzoyl peroxide presents a new chemical hazard distinct from untreated benzoyl peroxide. We know from this accident that in the F&HCIC Annex the treated benzoyl peroxide deposits have lasted on the order of 15 years and the deposition is extensive, leading to total blockage of the drain pipe. Further testing of the drain pipe down stream from the explosion site would seem to be appropriate to mitigate the potential for future injuries.

## How did benzoyl peroxide get in the pipes?

With no access to details of the history of the Ivorydale Fabric and Home Care Innovation Center prior to 1999, it is difficult to precisely determine the source of benzoyl peroxide in the drainpipes. The site has developed a wide range of consumer products including Cascade Plastic Booster<sup>®</sup>, mentioned above. It is believed that waste from development processes was disposed of using the floor drains over a number of years probably between 1989 and 1999 and until the drains became blocked due to buildup of the insoluble benzoyl peroxide. A series of photographs were taken during the two site visits in 2009 showing blocked drains near the accident site. Some of the drains appear to have been sealed on inspection and in the photographs taken at the scene, however the P&G attorneys indicate that they have no knowledge of the drains having been sealed. It is logical that the source of the explosive deposits was the improper disposal of treated benzovl peroxide waste from industrial development processes at the site. The situation may have been exacerbated by treatment, processing, or contamination of the benzoyl peroxide. Particularly, treatment with "nanoparticles", surfactants or encapsulation as well as manipulation of the benzoyl peroxide particle size could lead to changes in the solubility and the appropriateness of disposal methods such as using alkaline water to wash waste benzoyl peroxide down the floor drains. These treatment processes and compositions are described in U.S. Patents 5,663,113, 5,710,115, 5,763,378, 5,904,161, 6,306,219 and 6,440,920.

The floor drains became unusable at some point during the operation of the Center. Normal safety procedures would seem to suggest testing of the blockage in the floor drains of an industrial site handling potentially explosive materials in moderately large quantities. Such testing would certainly be expected prior to remediation of the blocked waste pipes given that benzoyl peroxide processing had been an activity of the facility at the time of the blockage and given the recent industrial accident in Ohio at U.S. Chemical and Plastics involving benzoyl peroxide.

#### How did an explosion occur?

In order for benzoyl peroxide to produce an explosion of the drainpipe, the aftermath being seen in photographs taken at the accident site, the explosive material had to be sealed in the pipe by a blocked floor drain (see photographs) as well as by blockage further downstream near the deposited benzoyl peroxide. The benzoyl peroxide ignited when the pipe temperature reached about 60 °C or when a spark was introduced, associated with cutting of the pipe. An inspection of the floor drains prior to removal should have indicated a potential hazard in that the drains were blocked; however, it could not have been anticipated that a potentially explosive material was present. Explosive solid deposits in the drainpipe could not have been easily foreseen without a detailed knowledge of the history of the site or an understanding of the rationale for removal of the drainpipes.

The opinions in this report are based on my education, training, and expertise in Chemical Engineering and Materials Science, and based on my inspection visits, chemical analyses, review of incident-related materials, and review of pertinent scientific and patent literature, and such opinions are stated to a reasonable degree of scientific and chemical engineering probability.

Dr. Gregory Beaucage Professor of Chemical and Materials Engineering University of Cincinnati Cincinnati OH 45221-0012 beaucag@uc.edu 513 556 3063

# Appendix A: References Used in This Report

# **Reports:**

Chemir Analytic Services Report Analysis Report #70687

Micrographs and Photographs from the Case Record

F&HCIC Chemical Hygiene Plan (Procter & Gamble)

Materials Safety Data Sheet for Benzoyl Peroxide

P&G Responses to 3 sets of Interrogatories and Requests for Documents P&G Responses to Requests for Admissions

Depositions:

Jeffery Painter Mark Wandstradt Frank Denome

# **P&G** Patents:

US Patent #	Application #	Filing	Issue	Title	Summary	Inventor
5,663,113	554,065	11/6/95	9/2/97	Process for Making Automatic Dishwashing Composition Containing Diacyl Peroxide	Dispersing agent for alkaline stabilization	A. S. Goldstein
5,710,115	713,043 continuation of 352,468	9/11/1996 continuation of 12/9/1994	1/20/98	Automatic Dishwashing Composition Containing Particles of Diacyl Peroxides	Stabilizing additive prevents di- benzoyl peroxide from degrading and protects it in alkaline conditions	R. N. Patel, E. P. Fitch V, J. D. Painter, A. S. Goldstein

5,763,378	627,821 continuation of 424,132	4/2/1996 continuation of 4/17/1995	6/9/98	Preparation of Composite Particulates containing Diacyl Peroxide for use in Dishwashing Detergent Compositions	Reduced benzoyl peroxide particle size in a carrier that melts at ~50°C to prevent degradation in alkaline conditions and in water	J. D. Painter, B. N. Wagner, M. D. Aquino
5,904,161	08/608,210	2/28/96	2/18/99	Cleaning Composition Containing Bleach and Stability- Enhanced Enzymes	Enzyme and banzyol peroxide in a powder detergent	S. Rai, W. M. Scheper, L. F. Taylor, G. S. Caravajal, J. C. Theophile, R. Burckettt- St. Laurent, K. Pramod
6,306,219	09/230,432	PCT 7/18/1997 US filing 1/25/1999 PCT Issue 1/29/1998	10/23/01	Method for Stain Removal on Hard Surfaces with Detergent Compositions Containing Bleach	Method to use a gel with benzyol peroxide to clean surfaces	K. Ofosu- Asante, H. D. Hutton
6,440,920	09/230,431	PCT 7/18/1997 US 1/25/1999 PCT Issue 1/29/1998	8/27/02	Sprayable, Liquid or Gel Detergent Compositions Containing Bleach	A gel with benzyol peroxide to clean surfaces	K. Ofosu- Asante, H. D. Hutton

# **Books and Papers:**

Handbook of Detergents Part D: Formulation, Michael S. Showell, CRC Press New York (2005).

A Comprehensive Guide to the Hazardous Properties of Chemical Substances, Patnaik P, Wiley Interscience, NY (2007).

OSHA Regulated Hazardous Substances: Health, Toxicity, Economic and Technological Data, U. S. Dept. of Labor, United States Occupational Safety and Health Administration, U. S. Dept. of Labor, William Andrew Inc. (1990).

Federal Register **68** 59777 (2003) Notices: Short untitled article on benzoyl peroxide explosion at Gnadenhutten Ohio on January 2, 2003.

International Agency for Research on Cancer (IARC)- Summaries & Evaluations CAS No. 94-36-0 Chem. Abstr. Name: Dibenzoyl peroxide **71** 345 (1999).

Dufault R, Abelquist E, Crooks S, Demers D, DiBerardinis L, Franklin T, Horowitz M, Petullo C, Sturchio G, *Reducing Environmental Risk Associated with Laboratory Decommissioning and Property Transfer* Environmental Health Perspectives **108** (2000) 1015.

Case Study U. S. Chemical Safety and Hazard Investigation Board Fire and Explosion: Hazards of Benzoyl Peroxide No. 2003-03-C-OH October 2003

Peroxides and Peroxide Forming Compounds Clark DE PhD Texas A&M University (2000).

Duh Y-S, Wu XH, Kao C-S *Hazard Ratings for Organic Peroxides* Process Safety Progress **27** 89-90 (2008).

# Web pages:

http://feedback.pgestore.com/pg\_estore/topics/looking\_for\_cascade\_plastic\_booster Indicates the date that P&G removed Cascade Plastic Booster from the market.

This is Google's cache of http://gis.wvdep.org/tri/cheminfo/csfs310.txt. It is a snapshot of the page as it appeared on Sep 12, 2008 02:33:26 GMT. The current page could have changed in the meantime.

#### **Appendix B: 2 Page CV**

#### **Gregory Beaucage**, Professor

Department of Chemical and Materials Engineering University of Cincinnati Cincinnati, OH 45221-0012 Office: 513 556-3063 Lab: 513 556-5152 Fax: 513 556-3473 e-mail: beaucag@uc.edu

http://www.eng.uc.edu/~gbeaucag/BeaucageResearchGroup.html

- 1980 <u>University of Rhode Island</u>, Kingston, RI 02881 *B.S. Zoology*; Highest Distinction. (National Merit Scholar Finalist, Elected to Phi Beta Kappa)
- 1982 <u>University of Rhode Island</u>, Kingston, RI 02881 **B.S.** Chemical Engineering; High Distinction. (Elected to Phi Kappa Phi)
- 1991 <u>University of Massachusetts</u>, Amherst, MA 01003 *Ph.D. Polymer Science and Engineering*. Advisor: *Richard S. Stein*. A Morphological, Mechanical and Thermodynamic Investigation of the Isotactic-PVME/PS Polymer Blend.
- 1991 <u>Sandia National Laboratory</u>, Albuquerque, NM 87185; *Post Doctoral Fellow*, Organic Materials Group *Characterization of nanomaterials using scattering & scattering theory*.

#### **Appointments**

- University of Cincinnati, Cincinnati, OH, 45221 *Professor*, Department of Chemical and Materials Engineering, 2008-present.
- <u>University of Cincinnati</u>, Cincinnati, OH, 45221 Associate Professor, Department of Chemical and Materials Engineering, 2000-2007.
- ETHZ, Zurich Switzerland Visiting Professor Funded by Swiss National Science Foundation and Dupont Corporation. 8/2003-8/2004.
- <u>University of Cincinnati</u>, Cincinnati, OH, 45221 *Assistant Professor*, Department of Materials Science and Engineering, 1994-2000.
- Sandia National Laboratory, Albuquerque, NM 87185, *Staff Member*, Organic Materials Group 1815. Cooperative research agreements with U.S. industrial partners. 1993-1994.
- US Patent and Trademark Office, Arlington, VA. Patent Examiner Biomedical Materials. 1982-1986.

#### **Other Experience and Professional Memberships**

2008 Fellow American Physical Society

- 2000-2008 Advisory Board Intense Pulse Neutron Source, Argonne Natonal Laboraotry.
- 2003-present Founding Member of LENS Neutron Scattering Facility at Indiana University
- 2000-present Founding Member of LSU Synchrotron CAMD SAXS User Group
- 1980-present Member American Institute of Chemical Engineers
- 1990-present Member American Physical Society
- 1992-present Member American Crystallographic Society
- 2004-2005 Chair of the Small Angle Scattering Special Interest Group ACryS.
- 2003-2004 Program Chair Small Angle Scattering Special Interest Group ACryS
- 1995-present Panel and Individual Referee for NSF/PRF/DOE/Commerce Proposals.

#### 10 Related Publications (from 113 peer reviewed H-Index 25)

- 1) Towards resolution of ambiguity for the unfolded state. Beaucage G Biophysical J. **95** 503-509 (2008).
- 2) Probing the dynamics of nanoparticle growth in a flame using synchrotron radiation. Beaucage G, Kammler HK, Mueller R, Strobel R, Agashe N, Pratsinis SE and Narayanan T, Nature Mater. **3**, 370-373 (2004).
- 3) In situ studies of nano-particle growth dynamics in premixed flames. Kammler HK, Beaucage G, Kohls DJ, Agashe N. Ilavsky J., J Appl. Phys. **97**(5) 2005 (Article 054309).
- 3D Hierarchical orientation in polymer-clay nanocomposite films. Bafna A, Beaucage G, Mirabella F Polymer 44, 1103-1115 (2003).
- 5) A structural model for equilibrium swollen networks. Sukumaran SK, Beaucage G Europhysics Letters **59** 714-720 (2002).
- 6) Approximations leading to a unified Synergistic Activities

- exponential/power-law approach to small-angle scattering. Beaucage G, J. Appl. Crystallogr. 28, 717-728 (1995).
- 7) Small-Angle Scattering from Polymeric Mass Fractals of Arbitrary Mass-Fractal Dimension. Beaucage G, J. Appl. Crystallogr. **29**, 134-146 (1996).
- 8) Determination of branch fraction and minimum dimension of mass-fractal aggregates. Beaucage G, *Phys. Rev. E*, **70**, 031401 (2004).
- 9) Quantification of branching in disordered materials. Kulkarni A, Beaucage G J. Polym. Sci. Polym. Phys. 44 1395-1405 (2006).
- 10) Persistence Length of Short-Chain Branched Polyethylene Ramachandran R, Beaucage G, Kulkarni AS, McFaddin D, Merrick-Mack J, Galiatsatos V Macromolecules In Press (11/2008).

1) Creation: Development of scattering theories (the unified function) to describe aggregate

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nanostructures, biopolymers, branched structures [1-4,6-10]. Integration: Pioneered application of x-ray scattering in situ to pyrolytic synthesis of nanomaterials [2,3]. Transfer of Knowledge: Developed and codeveloped user software for the analysis of scattering data using the unified function with Jan Ilavsky.

- 2) Creation: Developed aero-sol-gel reactor for room temperature aerosol synthesis.
- 3) Transfer of Knowledge: Chairman of small-angle scattering group American Crystallographic Association, Organizer for annual meeting of ACA.
- 4) Transfer of Knowledge: Organizer for characterization session in particle technology for AIChE meeting Fall 2005, and Spring (World Particle Congress) 2006. Organizing session on in situ characterization for Fall 2006 AICHE meeting in San Francisco. Organized three sessions for AICHE in Philadelphia 100'th Anniversary Annual Meeting 2008.
- 5) Transfer of Knowledge: 12 web courses (9 pertaining to polymers) extensive notes, lab experiments and data. 235,000 different IP#'s have hit this course suite since 2000 (averaging >70 IP hits/day).

#### Collaborators & Other Affiliations (past 48 months)

Dr. J. A. van Bokhoven, Professor, ETH, Chem. and Dr. S. K. Sukumaran, Assistant Professor, Bioengineering, Zurich, Switzerland. Yamamoto University Japan.

Switzerland.

Cincinnati OH

University of Cincinnati

Cape Town, South Africa

- Dr. J. Ilavsky, UNICAT, APS, Argonne National Dr. T. Trevoort, Materials Science, ETHZ, Zurich Laboratories, Argonne Illinois.
- Dr. F. Mirabella, Independent Consultant, Fort Vassilios Galiatsatos, Senior Scientist, LyodellBasell Myers Flordia.
- Dr. T. Narayanan, ESRF ID02, Grenoble France.
- Dr. S. E. Pratsinis, Process Engineering, ETHZ, Zurich, Switzerland.

#### Graduate & Postdoctoral Advisors

- Dr. Richard S. Stein, Emeritus Professor of Polymer Science and Engineering, University of Massachusetts, Amherst, MA. Member NAS and NAE.
- Dr. D. W. Schaefer, Professor of Engineering (Formerly Dean of Engineering), U. Cincinnati. Post-doc was with Schaefer and John Curro at Sandia National Laboratory.
- Dr. J. G. Curro, Former Head of Polymer Group, Sandia National Laboratory, Albuquerque NM.

Thesis Advisor and Postgraduate-Scholar Sponsor (PhD: 7, MS: 8, Post Doc: 2)

Current Students: (4 Graduate Students, 2 Funded Department (Minority teacher). Teacher, 2 Unfunded Undergraduates)

**Durgesh Rai:** PhD studies scattering theory.

Sachit Chopras: nanoparticles nano-catalysts and for applications. Funded by NSF CTS.

and persistence effects on rheology in polyolefins. Funded by LyondellBasell.

Ryan Breese (MS 2004; PhD 2009): PhD studies on oriented polymer film structure/property relationships. Funded by Equistar and now by Eclipse Film Technologies.

Mangesh Champhekar: (MS 11/2008) Studies of ultra oriented polyolefin/clay nano-composites.

Hao Liu, Senior Project: In situ SAXS studies of Diesel Exhaust at the CHESS Synchrotron.

Kurt Woodford, Senior Project: Orientation in Yamata University, Japan. Polyolefin Films.

Undergraduate Research Assistant (NSF REU Students): Stephanie Berger, Carbon coated silica Robin Holland, for solar cell applications. (Minority REU Student) In situ studies of diesel exhaust nanoparticulates using synchrotrons. Maesa Idries, Current REU student.

High School Teacher (NSF RET Participant): Edwin Segbefia Princeton High School Physics

Flame-made REU Undergraduate, 1 funded RET High School hematite nano-particles for arsenic remediation in drinking water.

Peter Smirnoitis, Professor Chemical Engineering,

David Britton, Professor Physics, University of

Select Past Graduated Students/Post Doc

PhD studies flame-made Amit Kulkarni (MS 2004; PhD 2007): Funded by other P&G, Intel, Equistar. Currently Research Engineer GE Plastics Evansville IN (10/2007).

Ramnath Ramachandran: PhD studies branching Doug Kohls, (MS 2002; PhD 2006): Currently Assistant Professor Dept. Materials Science and Engineering University of Cincinnati.

Hashard Chavan (MS 2006) Bioplastics San Jose CA.

Ayush Bafna (PhD 2004, MS 2002) Research Engineer, Dow Chemical Central Research Freeport TX.

Nikhil Agashe (PhD 2004, MS 2001) Research Engineer GE Plastics, Evanston IN.

Suresh Murugesan (PhD Chemistry 2003) Scientist Texas Research Institute.

S. Sukumaran (PhD 2002) Asst. Prof. Polymer Science

G. Skillas (Post-Doc from ETH Zurich 2001) Research scientist, GMX Degussa, Hanau Germany.

J. Hyeon-Lee (PhD 1998) Research Scientist, Samsung Research Institute, Seoul, South Korea.

Ling Guo (MS 1997) P&G Miami Valley Laboratories (Central Research Division).

S. Rane (PhD 1999) Senior Research Engineer, Procter& Gamble Beckett Ridge Technical Center Cincinnati.